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INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN THE EASTERN UNITED STATES. PHASE II. METEOROLOGICAL ANALYSES

W. D. Bach, Jr.

Research Triangle Institute

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INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN THE EASTERN UNITED STATES, PHASE II, METEOROLOGICAL ANALYSES

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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16. ABSTRACT

The meteorological conditions occurring during measurements of ozone at four nonurban locations in Ohio, Pennsylvania, Maryland and West Virginia are examined for their influence upon the ozone concentrations at the synoptic time and space scale. Air parcel trajectories at the 900 mb level for the forty-eight hours prior to arrival at each location were examined for the possible influence of transport across urban-industrial areas on the measured non-urban ozone. Time-altitude sections of potential temperature and stability from the ground to 5 km at four nearby rawinsonde locations showed that major anomalies in the vertical structure of the lower troposphere are important to the occurrences of high ozone concentrations. A regression analysis of twelve-hour average ozone concentrations as a function of properties of the mixed layer showed that the mean mixing ratio of the layer in the most significant variable of the eight shown. The mixing depth is the next most significant.

Average hourly ozone concentrations did not exceed 160 $\mu g/m^3$ when the maximum daily temperature was less than 16.5°C.

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INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN THE EASTERN UNITED STATES

PHASE II

INVESTIGATION SUMMARY

Background

From July through the end of October 1973, the Research Triangle Institute operated nonurban sampling locations at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia. At these locations, ozone, oxides of nitrogen, and hydrocarbons were monitored continuously to determine, in part, the areal extent of high ozone concentrations in nonurban areas of the northeastern United States; to provide a data base of nonurban ozone and ozone precursor concentration measurements for future detailed analysis; and to determine the interrelationship between ozone concentrations and its precursors at the selected locations. Subsequent to that field investigation, this program examined various meteorological conditions that accompanied these ozone concentrations, high and low, attempting to relate the aerological and air quality measurements at or near these four monitoring locations. The primary emphasis of the meteorological portion of the study is at the synoptic scale--the scale of motions that produce the day-to-day weather changes.

Analysis Techniques

Three primary methods of analysis were adopted:

1) The time-altitude sections of potential temperature and significant temperature layers were developed showing some of the dynamical processes of the lower atmosphere where the ozone is generated and transported. The relationship of inversions and/or fronts and atmospheric structure to the twelve-hour average ozone concentration changes were examined at each of the four locations using those sections.

2) Trajectories, approximating the path of air parcels during the 48-hours prior to their arrival, were computed for each location at each twelve-hour interval during the field study. These trajectories were examined for their association with high or low concentrations and the

implications as to the existence of preferred "source" regions (urban or nonurban) as indicated by the spatial distribution of hydrocarbon emission density.

3) The statistical relationships of the twelve-hour ozone concentrations to the properties of the mixing layer (usually confined within the lowest 2 km) of the atmosphere at rawinsonde locations near the nonurban sites were investigated. Correlation coefficients and the significance of the meteorological parameters upon the ozone concentrations were determined.

Interpretation and Results

In earlier studies, data had indicated that ozone concentrations tended to rise steadily prior to frontal passage and decrease rapidly, apparently in association with the frontal passage. Thus, either the high ozone concentrations were associated in some way with the frontal passage, or they were associated with the characteristics of the air mass before and after the frontal passage. There are several ways to investigate the relationships of ozone with frontal passages in the 1973 data. At the same time, properties of the air masses before and after the frontal systems and other properties of the lower atmosphere where turbulence and transport of ozone are taking place can be investigated. Some studies have also suggested that high ozone concentrations at the ground or perhaps even at nighttime might be associated with inversion layers aloft, which effectively limit the vertical dispersion of pollutants.

Time-altitude sections were plotted with potential temperature (an indicator of the state of the atmosphere), the date and time of frontal passages, and the twelve-hour average ozone concentrations on the same time axis for each of the four nonurban locations. Although changes in ozone concentration were occasionally related to the frontal passages, only the major disturbances of potential temperature shown in the cross-sections were associated with the changes of the ozone concentrations. In many instances of frontal passages, the potential temperature sections suggested that hardly any changes of air masses took place. No major trends of ozone concentrations developed before or after these frontal passages. An association of high and low ozone concentrations before and after some frontal passages were evident principally during early July and in October at Kane. The effects of those fronts could not be documented at the other locations, since Kane was the only operative monitoring location at those times.

The time sections clearly show the atmospheric changes--slowly descending, stabilizing motion, and strong warming aloft--through the lower 5 km of the atmosphere accompanying the onset of a stagnant weather system along with a major increase of ozone concentration during day and night. During the latter part of an eleven-day episode in late August and early September at McHenry, those stagnant conditions remained, but descending motion gave way to much less stable conditions. The ozone concentration decreased at a slow rate, although deep vertical mixing was possible. Similar weather conditions existed over the study area, but each locality showed somewhat different trends of the ozone concentrations. The subsiding motion was too weak and short lived to have transported ozone downward from the stratosphere to account for the high ozone concentrations.

On the basis of these analyses, it became apparent that ozone concentrations change when there are major disturbances in the atmospheric structure--extending above 2 km--but local factors, perhaps terrain, also influence the daily trends of ozone.

A most elementary concept of high ozone concentrations might be to consider that metropolitan and industrial areas are the most likely anthropogenic sources of ozone precursor materials. Downwind of those cities, precursors are mixed together and form ozone in sunlight. From simple dispersion models, the ozone concentration would be expected to be directly proportional to the emissions of precursor material and inversely proportional to the wind speed, i.e., the highest ozone concentrations should be associated with air that moves slowly over major source areas. To test that overall concept, air parcel trajectories, indicative of the path that air near the ground has taken for the past forty-eight hours, were computed for each of the nonurban locations from upper air data. If high ozone concentrations at the nonurban locations were related to specific anthropogenic source regions upwind of the station, then the trajectories with the high ozone concentrations should pass over those specific sources. By the same reasoning, low ozone concentrations might be associated with trajectories that have a small residence time (higher speed) over areas of low emissions. On both counts, the trajectory analysis fails to show consistent association of high ozone and high emission densities, or low ozone and low emission density. Specific source regions for the occurrences of high or low ozone concentrations at any of the four nonurban ozone monitoring locations could not be identified. These data suggest that the high ozone concentrations were associated with slower-moving air, especially the prolonged stagnation period in late August and early September, and that low ozone concentrations were associated with faster moving air. Hence, one concludes that the trajectory that the air takes en route to each of the four ozone monitoring locations, influences but does not determine the extent of the ozone concentration.

The trajectories relate to the horizontal transport of ozone or ozone precursors; the potential temperature sections relate to the synoptic motion producing changes in the vertical structure of the atmosphere. The mixed layer--the layer of the air near the ground influenced by the daily radiational heating and cooling--is important to the turbulent dispersion of ozone or ozone precursors. The mixed layer varies from day to night and as the weather systems move through. The response of the layer to these influences is given by the variability of its properties, e.g., mixing depth, ventilation, relative dispersion, mean wind velocity, and mean water vapor content. The relationship of those properties to the comparable term ozone concentration were examined.

The linear correlation coefficients of the ozone concentrations (measured at a nonurban site) and the mixed layer parameters (measured at a nearby urban rawinsonde location) were computed. In only two instances did the magnitude of correlation exceed 0.30 with a variable other than the time of day, the mixing depth, or the water vapor mixing ratio. The correlation of water vapor mixing ratio with ozone was the only one to have the same sign (positive) in all cases.

The best combined linear regression of all mixed layer properties with the ozone showed that the water vapor mixing ratio and mixing depth were usually the most significant terms of the regression. These results suggest that high ozone concentrations are associated with high water vapor content--an unexpected finding. The physical significance of the statistical finding is not yet understood.

Another study showed that a high linear correlation exists between the maximum hourly ozone concentration for the day at the nonurban locations and the daily maximum temperature at a nearby location.

INVESTIGATION OF OZONE AND OZONE PRECURSOR CONCENTRATIONS AT NONURBAN LOCATIONS IN THE EASTERN UNITED STATES

PHASE II

1.0 INTRODUCTION

Until recent years, ozone, as an air pollutant, was considered as an urban problem resulting from photochemical reaction of emitted reactive hydrocarbons and oxides of nitrogen. Dilution with nonurban air during transport and destructive mechanisms were thought to reduce the concentrations in nonurban areas.

In the course of a study of injury to Christmas trees, Environmental Protection Agency (EPA) investigators were surprised to find oxidant concentrations at sites in western Maryland and eastern West Virginia frequently exceeding the National Ambient Air Quality Standard (NAAQS) for ozone (160 $\mu g\ m^{-3}$) during the period May 29 through September 28, 1970.[1] Corroborative measurements made with a chemiluminescent ozone meter showed that virtually all of the oxidant at one site was ozone.[2] Of particular interest was the fact that the high ozone concentrations persisted into the dark hours; i.e., ozone concentration did not exhibit the typical diurnal pattern in which it decreases to near zero at night. Nitrogen oxide concentrations during this period were reported to be near background levels.[2]

Ozonesonde measurements have shown that ozone-rich layers occur within elevated but low-level inversion layers.[3] The high ozone concentrations observed aloft at Point Mugu, California, can be attributed to precursors originating in the Los Angeles area. The transport of photochemical smog from Fresno to the Mineral King Valley of California has been suggested.[4]

Miller and Ahrens[5] showed locally high ozone concentrations below the West Coast inversion could be associated with breaks or folds in the inversion over San Francisco Bay. Further inland, where and when the inversion is dissipated by surface heating, ozone concentrations increased rapidly at the ground and increased aloft during the day. At night, ozone aloft, insulated from the ground by the reestablished inversion, showed small decreases of concentration. High ozone concentrations were found in unstable air; and low ozone concentrations in stable air.

Vukovich[6] and others showed diurnal changes of ozone concentration at ground level and aloft are strongly influenced by the onset of radiative inversions and hence, air stability. These studies implied only slight nocturnal decreases in ozone concentrations above the inversion layer.

Ozone concentrations measured at Indio, California 140 miles from Los Angeles, exceeded the air quality standards for oxidants more frequently than at any other sampling site in California. The high concentrations occur during day and night hours.[7] The evidence indicates that transport to Indio from the Los Angeles Basin is a contributing factor to the observed concentrations.

Analysis of episodes of ozone concentrations exceeding the NAAQS near Miami, Florida showed that long-range transport of the ozone or ozone precursors may have been responsible.[8]

RTI's 1972 study[9] of ozone concentrations at McHenry, Maryland identified increases of ozone during day and night when high pressure systems stagnated in the northeastern United States. These episodes ended rather abruptly as frontal systems moved through the area, replacing the stagnant air with air having a different history. Approximate air trajectories at the 850-mb pressure surface indicated that episodes of high ozone concentrations at McHenry were associated with air which had previously moved over the urban-industrial areas of the lower Great Lakes and the mid-Atlantic States.

RTI's 1973 field study and analyses[10] (Phase I of this contract) sought to establish a data base of nonurban ozone and ozone precursor concentrations at four locations in the northeastern United States; to develop statistical summaries of the frequency of occurrence of ozone, nitrogen dioxide, and non-methane hydrocarbons at those locations; and to determine interrelationships between ozone concentrations and ozone precursor concentrations at the locations. During this study, an EPA aircraft equipped with an ozone meter made two flights over the study area. Ozone concentration measurements were taken enroute to each station, where a low altitude fly-by of the ground stations was made. Profiles of ozone concentrations during descent and ascent and a near-ground check of the two ozone measurements were obtained. The validity of measurements at each ground station was checked as part of a data quality assurance program.

The statistical summaries show that the hourly average ozone concentrations repeatedly exceeded the NAAQS for ozone. The frequency of occurrence of hourly concentrations in excess of the ozone standard at McHenry was 37 percent in 1973, in comparison to 11 percent found in 1972. Lag correlation studies between stations gave correlation coefficients of 0.468 to 0.678. These data reinforced the conclusion that the occurrence of high ozone concentrations at nonurban locations is widespread, affecting a large area in the eastern United States.

Analysis of the airborne measurements indicated that high ozone concentrations were prevalent over much of the study area; that horizontal and vertical gradients of ozone concentrations existed aloft; and that the ozone concentrations tend to persist.

Previous studies have investigated only a few of the possible meteorological influences upon the ozone concentrations that are observed in these nonurban areas over the northeastern United States. This research expands upon those studies. It investigates the meteorological conditions present during the study period, tries to relate them to the observed ozone concentrations at the nonurban locations, and tries to find the influence of possible sources of ozone or ozone precursors.

The areal coverage and magnitude of the problem over the industrialized east is not directly analogous of the problem of photochemical smog in the Los Angeles Basin. Indeed, it represents a different problem with a complex interaction of various source areas, atmospheric dispersion in different terrain conditions, and finally, is subject to transient weather systems.

2.0 OBJECTIVES

In this study, the various meteorological conditions are quantified and related to the average ozone concentrations at each of the four monitoring sites. The conditions are documented through observations made at National Weather Service Offices. From these data, the meteorological variables that have a strong or weak influence upon the measured ozone concentrations are determined. The documentation is concerned with horizontal and vertical distribution of the meteorological variables. Some of the synoptic weather characteristics investigated are: time sections of the vertical structure of the lower troposphere; the characteristics of the mixing layer which affect the dispersion and transport of pollutants; and the characteristics of fronts and pressure systems.

Another objective is to develop and analyze air parcel trajectories arriving at each of the sampling sites and relate them to the occurrences of high or low ozone concentration at the nonurban locations. Investigation of low ozone concentrations is as important as that of high ozone cases if geographic or meteorological differences are to be examined.

The magnitude of ozone concentrations observed during 1973 were different from those observed in 1972, suggesting that climatic variables, e.g., temperature, precipitation, sunshine, or pressure-system movement, during 1973 were substantially different than in 1972. An examination of these differences was another research objective.

Finally, in the process of the investigation, certain avenues of research appeared promising in explaining the high or low ozone concentration. Some of these were pursued in an effort to give the research as broad a scope of possible.

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3.0 DATA SOURCES

3.1 Ozone Data

The ozone data for this study were taken during the field monitoring program conducted by RTI in the summer and early fall of 1973 at four ozone monitoring locations at Kane, Pennsylvania, McHenry, Maryland, Lewisburg, West Virginia and Coshocton, Ohio (Figure 1). The gathering, reduction, and tabulation of these data have been documented and reported.[10] The basic unit of the ozone data provided for analysis was the one-hour average concentration.

3.2 Meteorological Data

3.2.1 Upper Air Data

Upper air data for each of twenty-two rawinsonde sounding stations within the northeastern United States were obtained from the National Climatic Center for the period July 1 through October 31, 1973. Two soundings are made daily at 0000 and 1200 Greenwich Mean Time (GMT). For each processed sounding the reported data include the altitude, pressure, temperature, relative humidity, wind speed and direction at 50-mb vertical increments and at any intermediate significant levels within the troposphere.

The location of most of the rawinsonde stations are also shown in Figure 1.

Four rawinsonde stations--Pittsburgh, Pennsylvania (PIT); Buffalo, New York (BUF); Huntington, West Virginia (HTS); and Dayton, Ohio (DAY)--were chosen as upper air stations "representative" of the McHenry, Kane, Lewisburg, and Coshocton ozone monitoring stations, respectively, principally because they were the closest upper air stations.

3.2.2 Surface Weather Observations

Surface synoptic meteorological data were derived from surface pressure analyses for three-hour increments during the period July 1 through September 30. These analyses show the movement and extent of high and low pressure systems, frontal systems, cloud amounts, and precipitation systems. Additional surface weather information was obtained from the Local Climatological Data Summaries (LCD) for numerous locations throughout the study area shown in Figure 1. Additional surface

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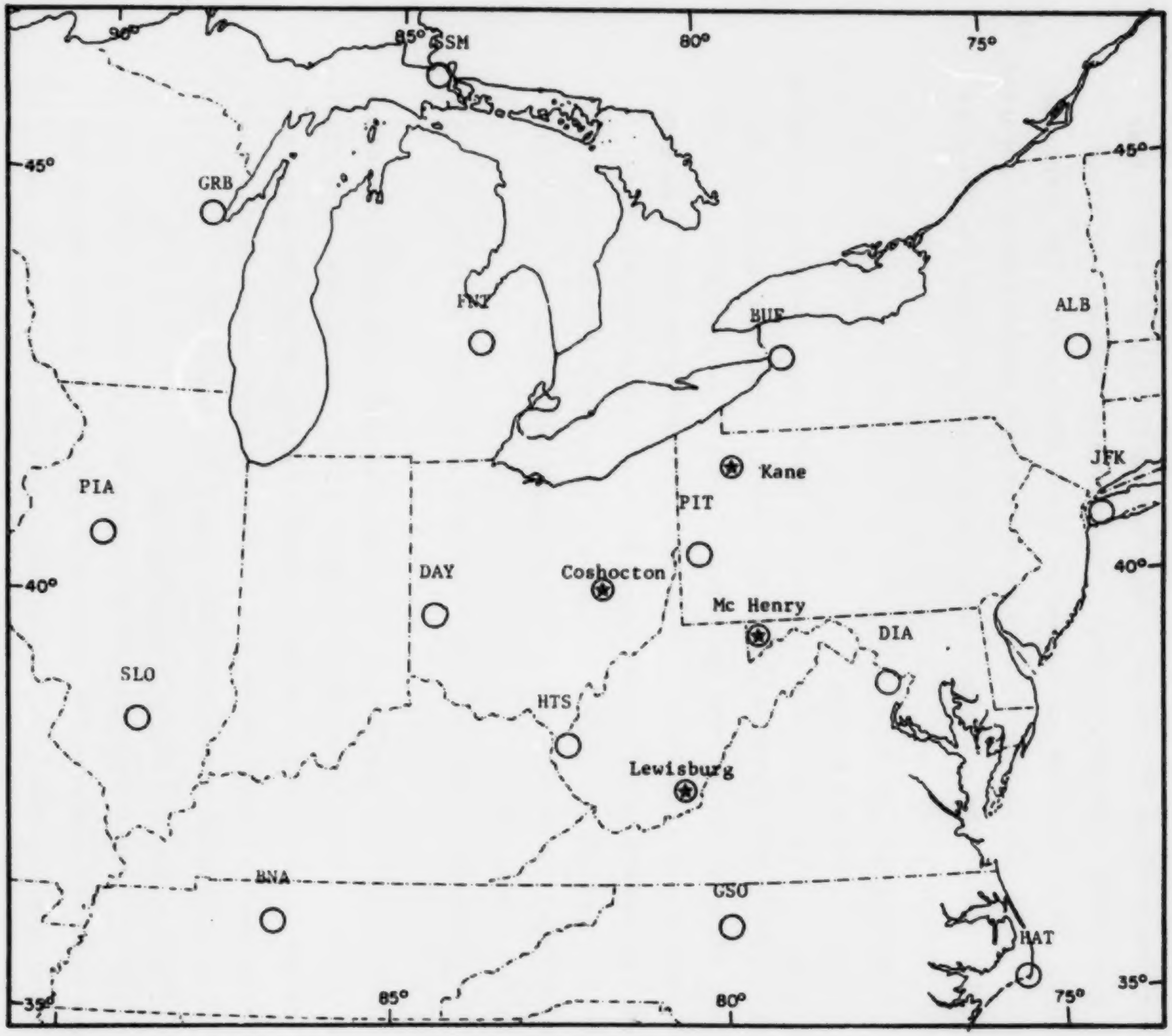
90°
85°
SSM
80°
75°
45°
GRB
FNT
BUF
ALB
PIA
Kane
JFK
PIT
40°
DAY
Coshocton
Mc Henry
DIA
SLO
HTS
Lewisburg
BNA
GSO
HAT
35°
85°
80°
75°

Figure 1. Location of ozone monitoring stations (⊛) and some rawinsonde data stations (○) used in the study.

pressure information was obtained from the Climatological Data National Summary. This publication gives analyses of the tracks of cyclones and anticyclones across the United States during each month.

4.0 OZONE CONCENTRATIONS AND SYNOPTIC WEATHER

4.1 Ozone Averaging Periods

Twelve-hour average ozone concentrations were computed for each of the four monitoring stations. The averaging period conforms to the minimum interval between rawinsonde releases. The rawinsonde data are the only routine measurements of the state of the atmosphere above the ground within the six hours prior until six hours following that observation. They define the minimum spatial and time resolution of synoptic scale motion aloft. Ozone concentrations averaged over the same period lose detail on the intradiurnal structure, but show longer term trends of ozone concentrations. The changes which occur in the longer term averages are more likely in response to the slowly changing synoptic meteorological conditions, depicted by the changes in the upper air observations. In earlier studies, the long-term trends of the ozone concentration with the synoptic meteorological conditions, were well depicted using this technique.

The averaging periods began at 0600 GMT (0200 EDT) and at 1800 GMT (1400 EDT) and continued for the following twelve hours. The former period corresponds to a twelve-hour interval centered about 1200 GMT whereas the latter interval is centered about 0000 GMT. These central times coincide with the times of rawinsonde observations. During the latter time period, the daily maximum ozone concentrations are usually observed. The 1200 GMT average value is usually lower, being associated with the nighttime and early morning hours, as indicated in Figure 2. These averaging intervals give a larger difference between twelve-hour average ozone concentrations than would have been found using daylight (0800-2000 EDT) and dark (2000-0800 EDT) averaging intervals.

Table 1 gives these twelve-hour averages for each station by months from July through October. At least six one-hour averages in one period were required to compute a twelve-hour average.

4.2 Frontal Analyses

The date and hour of each frontal passage at the four ground observing stations was determined from the surface pressure analyses. The type, intensity, characteristics of each front, as coded on the analyses, were recorded. The speed and direction of frontal movement was computed from the maps. This information is presented in Table 2. In all of the cases,

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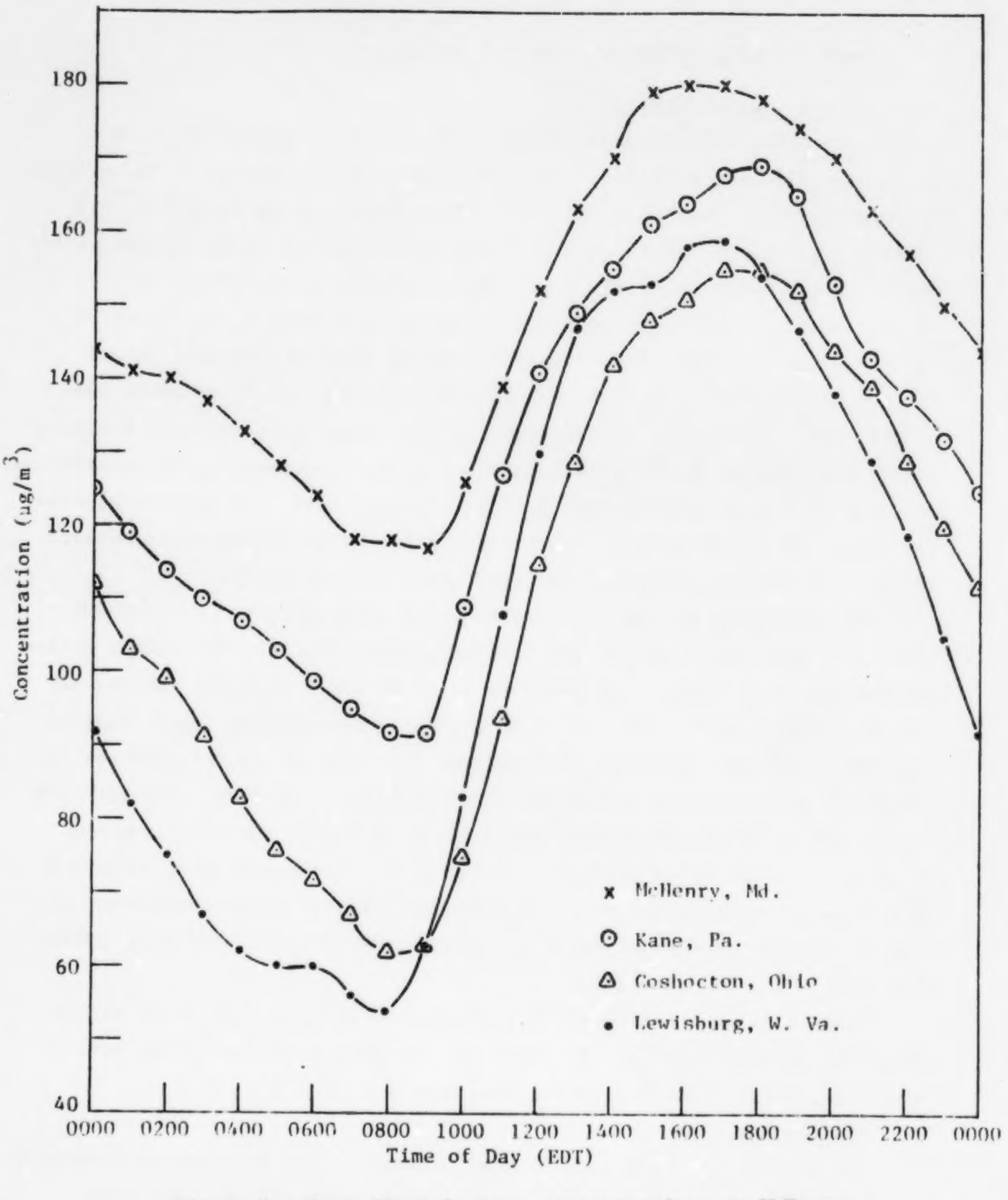


Figure 2. Mean diurnal ozone concentrations at McHenry, Maryland; Kane, Pennsylvania; Coshocton, Ohio; and Lewisburg, West Virginia, from June 26 to September 30, 1973.[10]

Table 1. TWELVE-HOUR AVERAGE OZONE CONCENTRATIONS

	1800 TO 0545 GMT				0600 TO 1745 GMT			
DATE	MC HENRY	KANE	COSHOCTON	LEWISBURG	MC HENRY	KANE	COSHOCTON	LEWISBURG
701	999.9*	168.6	999.9	999.9	999.9*	131.6	999.9	999.9
702	999.9	184.8	999.9	999.9	999.9	111.7	999.9	999.9
703	999.9	191.9	999.9	999.9	999.9	101.1	999.9	999.9
704	999.9	152.7	999.9	999.9	999.9	118.7	999.9	999.9
705	999.9	146.0	999.9	999.9	999.9	101.2	999.9	999.9
706	999.9	96.0	999.9	999.9	999.9	119.2	999.9	999.9
707	999.9	186.9	999.9	999.9	999.9	152.5	999.9	999.9
708	999.9	208.7	999.9	999.9	999.9	192.4	999.9	999.9
709	999.9	223.2	999.9	999.9	999.9	191.7	999.9	999.9
710	999.9	126.8	999.9	999.9	999.9	91.1	999.9	999.9
711	999.9	101.3	999.9	999.9	999.9	77.6	999.9	999.9
712	999.9	88.3	999.9	999.9	999.9	66.5	999.9	999.9
713	999.9	106.6	999.9	999.9	999.9	98.5	139.0	999.9
714	999.9	230.6	229.1	120.2	999.9	173.9	174.8	108.2
715	999.9	135.0	198.3	172.6	999.9	104.9	114.2	999.9
716	999.9	117.1	154.5	999.9	999.9	79.2	72.0	999.9
717	999.9	109.9	129.1	999.9	999.9	87.5	83.0	999.9
718	999.9	145.5	177.6	120.3	999.9	157.9	94.3	91.4
719	999.9	219.8	190.9	135.3	999.9	165.3	167.6	80.8
720	999.9	215.4	181.7	96.9	990.9	180.6	71.7	63.8
721	999.9	167.5	85.5	96.0	999.9	113.3	87.6	72.1
722	999.9	94.7	87.6	99.9	999.9	67.8	56.5	68.0
723	999.9	85.1	122.0	91.5	999.9	99.6	58.9	64.8
724	999.9	140.6	154.3	116.8	999.9	137.7	59.0	131.9
725	222.5	141.0	85.3	107.7	133.6	90.2	57.0	71.6
726	149.9	103.0	132.2	108.6	132.9	114.2	999.9	85.1
727	136.4	156.3	89.9	103.7	135.4	101.8	85.8	73.5
728	156.0	135.1	125.6	91.9	142.3	100.3	86.7	65.5
729	179.6	148.7	105.4	97.5	107.8	69.8	39.0	94.3
730	129.9	61.4	103.3	99.5	132.7	81.2	75.5	46.7
731	188.2	142.9	163.4	92.4	163.8	116.7	84.0	64.1

*999.9 - insufficient data

Table 1 (continued).

DATE	1800 TO 0545 GMT				0600 TO 1745 GMT			
	MC HENRY	KANE	COSHOCTON	LEWISBURG	MC HENRY	KANE	COSHOCTON	LEWISBURG
801	148.0	160.8	102.4	90.1	114.3	93.0	74.6	49.1
802	114.7	115.6	111.4	49.8	125.2	120.3	71.2	60.6
803	174.4	163.1	113.7	125.2	117.5	132.0	67.2	53.6
804	209.3	102.0	130.0	88.1	138.1	80.7	71.6	63.3
805	218.4	83.7	135.4	108.0	149.6	102.0	125.5	76.6
806	201.4	154.0	152.5	117.0	161.5	169.2	145.9	70.7
807	163.3	232.1	187.7	90.9	127.4	139.2	112.1	74.9
808	165.2	189.7	159.2	97.0	135.9	134.4	103.7	53.4
809	213.4	274.6	137.8	84.3	163.1	196.0	69.3	61.6
810	180.6	285.9	124.8	126.5	137.7	158.4	43.9	26.8
811	116.5	220.4	90.6	999.9	122.6	152.5	61.5	999.9
812	155.3	219.0	107.8	999.9	127.9	136.8	80.2	999.9
813	158.7	160.9	107.5	999.9	115.5	133.0	32.4	999.9
814	111.4	147.5	75.1	88.4	109.1	133.8	39.7	59.8
815	115.1	152.5	87.7	84.2	108.4	147.4	77.1	92.9
816	127.7	203.0	116.3	135.5	127.3	169.7	62.1	112.6
817	156.1	162.1	138.6	170.0	147.2	167.2	69.9	141.5
818	147.9	216.2	109.6	172.6	137.3	166.9	119.7	157.4
819	208.7	184.5	149.7	219.6	153.0	160.7	105.4	144.6
820	176.9	176.0	116.3	214.4	138.7	137.2	50.6	122.4
821	99.5	200.1	80.7	156.6	89.2	140.5	41.1	94.8
822	108.3	115.5	42.6	109.4	32.3	41.9	29.5	98.2
823	115.7	87.3	76.9	142.9	110.2	89.2	33.0	90.5
824	188.3	86.0	167.1	145.7	140.3	86.6	176.3	72.1
825	164.7	108.3	110.0	999.9	145.1	118.7	79.7	999.9
826	177.1	171.7	158.0	999.9	175.7	159.2	147.2	999.9
827	202.4	231.2	283.4	132.1	208.5	140.2	330.3	86.1
828	273.0	195.6	348.1	176.8	224.5	150.6	216.1	124.1
829	313.7	184.8	208.2	185.4	244.3	223.1	143.5	110.9
830	294.9	221.2	185.6	130.9	277.9	178.6	178.6	90.3
831	236.9	197.8	211.6	189.4	228.6	125.5	100.5	114.3

Table 1 (continued).

DATE	1800 TO 0545 GMT				0600 TO 1745 GMT			
	MC HENRY	KANE	COSHOCTON	LEWISBURG	MC HENRY	KANE	COSHOCTON	LEWISBURG
901	222.7	168.2	174.3	185.7	184.5	139.8	117.8	96.2
902	248.4	157.5	152.7	151.3	219.0	153.0	130.8	108.3
903	275.3	127.6	175.3	138.1	165.8	107.9	135.7	101.6
904	192.0	159.2	188.3	191.4	199.1	118.5	142.0	101.7
905	194.9	999.9	212.7	159.2	190.9	999.9	82.2	100.9
906	175.3	185.5	139.8	118.9	150.3	120.8	97.9	100.2
907	154.0	145.6	117.8	169.1	112.8	88.5	46.4	149.0
908	163.6	117.2	122.8	202.7	131.8	114.6	88.4	92.4
909	176.2	111.5	130.6	134.6	98.2	73.2	51.9	62.4
910	75.9	93.2	80.8	93.3	77.3	81.1	60.6	67.9
911	127.4	178.3	138.9	91.0	143.3	93.5	57.5	69.7
912	159.1	102.7	126.8	149.6	102.2	60.1	60.3	106.6
913	131.3	75.7	91.7	124.3	96.3	80.9	50.7	79.8
914	151.1	124.1	139.5	158.6	129.5	115.1	91.4	93.7
915	91.7	999.9	999.9	100.9	93.9	999.9	999.9	90.5
916	152.6	999.9	999.9	111.5	137.0	999.9	999.9	63.5
917	120.8	999.9	999.9	110.6	59.7	999.9	999.9	71.1
918	113.6	70.1	999.9	136.2	83.4	65.6	999.9	81.1
919	44.3	60.3	79.9	62.6	78.3	67.1	55.0	52.0
920	116.8	105.9	93.9	104.8	107.8	51.5	59.2	55.7
921	127.7	43.4	74.1	100.1	51.9	65.3	50.6	66.9
922	64.5	105.7	111.8	135.7	113.6	70.7	91.6	133.8
923	213.7	151.1	146.0	127.4	126.3	85.0	81.9	92.8
924	153.2	140.8	104.3	112.0	149.9	57.5	66.9	65.7
925	158.0	99.2	135.5	116.8	115.1	73.0	67.7	91.5
926	146.5	75.3	142.2	140.8	125.7	88.8	103.8	129.4
927	140.3	133.5	128.6	118.3	118.0	86.8	80.2	79.5
928	170.4	193.6	149.3	82.5	151.6	92.2	67.3	49.9
929	174.5	70.3	110.0	104.0	89.3	46.4	36.7	50.4
930	95.5	48.7	39.6	69.8	73.0	53.2	35.9	48.8

Table 1 (continued).

DATE	MC HENRY	1800 TO 0545 GMT KANE	COSHOCTON	LEWISBURG	MC HENRY	0600 TO 1745 GMT KANE	COSHOCTON	LEWISBURG
1001	101.7	76.5	59.2	67.9	86.3	73.1	31.6	83.2
1002	95.6	95.9	62.6	78.8	73.8	58.9	36.0	58.6
1003	71.9	59.6	93.5	77.3	98.0	76.1	61.6	42.1
1004	999.9	158.7	133.8	112.2	999.9	152.7	48.0	65.9
1005	999.9	169.8	101.1	109.4	999.9	135.6	61.0	69.0
1006	999.9	145.0	89.4	86.4	999.9	135.2	43.4	54.5
1007	999.9	184.9	79.7	98.0	999.9	128.2	48.9	62.1
1008	999.9	131.4	107.7	97.1	999.9	132.5	44.6	46.2
1009	999.9	203.6	89.8	68.0	999.9	143.8	46.8	49.6
1010	999.9	180.9	122.2	85.5	999.9	128.3	76.1	55.1
1011	999.9	164.5	150.5	92.4	999.9	145.4	48.5	62.8
1012	999.9	176.6	109.1	111.9	999.9	121.5	69.2	82.2
1013	999.9	216.6	122.3	101.6	999.9	150.1	68.7	68.9
1014	999.9	194.6	70.7	118.2	999.9	143.9	57.4	87.9
1015	999.9	153.8	79.2	87.9	999.9	96.0	64.4	81.7
1016	999.9	134.6	87.5	115.6	999.9	117.0	59.9	100.2
1017	999.9	118.9	67.1	90.7	999.9	89.0	52.5	68.1
1018	999.9	48.9	66.3	76.0	999.9	37.4	46.4	64.9
1019	999.9	64.4	63.5	112.1	999.9	53.2	47.1	67.0
1020	999.9	60.4	65.4	96.0	999.9	49.1	63.7	81.7
1021	999.9	59.5	65.5	124.3	999.9	65.0	39.8	70.9
1022	999.9	116.2	76.5	129.8	999.9	98.2	45.9	69.8
1023	999.9	119.5	115.0	999.9	999.9	109.0	62.0	999.9
1024	999.9	139.5	158.4	137.0	999.9	129.5	129.6	88.2
1025	999.9	148.5	999.9	113.4	999.9	121.7	999.9	68.2
1026	999.9	169.2	999.9	81.2	999.9	129.9	999.9	65.9
1027	999.9	71.2	999.9	101.5	999.9	42.2	999.9	75.9
1028	999.9	63.4	999.9	114.6	999.9	63.8	999.9	98.2
1029	999.9	76.7	999.9	94.1	999.9	83.3	999.9	56.7
1030	999.9	81.5	999.9	50.5	999.9	49.7	999.9	29.8
1031	999.9	999.9	999.9	36.2	999.9	21.1	999.9	63.7

Table 2. SUMMARY OF FRONTAL CHARACTERISTICS

DATE	HR	LOCATION	DIR	SP	TYPE	INTENSITY		CHARACTER
JUL 3	12	COSHOCTON	W	8.3	COLD	WEAK	N C	DIFFUSE
JUL 3	15	KANE	W	10.4	COLD	WEAK	N C	DIFFUSE
JUL 3	20	MC HENRY	NW	8.8	COLD	WEAK	N C	DIFFUSE
JUL 4	2	LEWISBURG	N	9.0	COLD	WEAK	N C	DIFFUSE
JUL 4	15	COSHOCTON	W	17.6	WARM	WEAK	DECR	DIFFUSE
JUL 4	15	LEWISBURG	SW	8.3	WARM	WEAK	DECR	DIFFUSE
JUL 5	2	COSHOCTON	NW	7.6	COLD	WEAK	N C	DIFFUSE
JUL 5	6	KANE	NW	7.9	COLD	WEAK	N C	DIFFUSE
JUL 5	11	MC HENRY	NW	13.2	COLD	WEAK	N C	DIFFUSE
JUL 5	12	LEWISBURG	NW	8.6	COLD	WEAK	N C	DIFFUSE
JUL 9	20	COSHOCTON	N	4.6	COLD	WEAK	N C	DIFFUSE
JUL 9	16	KANE	N	5.6	COLD	WEAK	N C	
JUL 11	10	MC HENRY	NW	14.4	COLD	WEAK	N C	DIFFUSE
JUL 11	11	LEWISBURG	NW	22.0	COLD	WEAK	N C	DIFFUSE
JUL 10	3	COSHOCTON	S	2.5	STAT	WEAK	N C	DIFFUSE
JUL 10	14	COSHOCTON	N	3.0	STAT	WEAK	N C	DIFFUSE
JUL 10	16	COSHOCTON	S	13.0	STAT	WEAK	N C	WITH WAVES
JUL 11	1	COSHOCTON	N	1.4	WARM	WEAK	N C	DIFFUSE
JUL 15	1	COSHOCTON	N	5.1	STAT	WEAK	N C	WITH WAVES
JUL 14	19	KANE	N	1.9	COLD	WEAK	N C	
JUL 15	16	MC HENRY	NW	4.6	COLD	WEAK	N C	WITH WAVES
JUL 15	20	LEWISBURG	NW	10.6	COLD	WEAK	N C	DIFFUSE
JUL 21	2	COSHOCTON	NW	5.3	COLD	WEAK	N C	
JUL 21	2	KANE	NW	9.5	COLD	WEAK	N C	
JUL 21	19	MC HENRY	N	5.3	COLD	WEAK	N C	WITH WAVES
JUL 22	22	LEWISBURG	NE	3.2	STAT	WEAK	N C	WITH WAVES
JUL 25	7	KANE	SW	23.6	WARM	WEAK	N C	DIFFUSE
JUL 27	6	COSHOCTON	NW	6.9	COLD	WEAK	N C	DIFFUSE
JUL 27	9	KANE	NW	10.9	COLD	WEAK	N C	DIFFUSE
JUL 27	18	MC HENRY	NW	10.4	COLD	WEAK	N C	DIFFUSE
JUL 27	20	LEWISBURG	NW	10.4	COLD	WEAK	N C	DIFFUSE
JUL 28	14	COSHOCTON	NW	13.0	COLD	WEAK	DECR	DIFFUSE
JUL 28	16	KANE	NW	3.2	COLD	WEAK	N C	
JUL 29	5	MC HENRY	NW	5.6	COLD	WEAK	N C	
JUL 29	7	LEWISBURG	NW	14.1	COLD	WEAK	N C	WITH WAVES
JUL 29	2	COSHOCTON	NW	6.2	COLD	WEAK	DECR	DIFFUSE
JUL 29	6	KANE	NW	3.5	COLD	WEAK	DECR	DIFFUSE
AUG 1	14	COSHOCTON	NW	3.9	COLD	WEAK	N C	
AUG 1	21	KANE	W	4.9	COLD	WEAK	N C	
AUG 2	2	MC HENRY	W	6.9	COLD	WEAK	N C	DIFFUSE
AUG 2	3	LEWISBURG	W	8.8	COLD	WEAK	N C	DIFFUSE
AUG 11	1	COSHOCTON	NW	7.6	COLD	WEAK	N C	DIFFUSE
AUG 11	7	KANE	NW	4.4	COLD	WEAK	N C	DIFFUSE
AUG 12	12	COSHOCTON	N	13.4	COLD	WEAK	N C	DIFFUSE
AUG 12	12	KANE	N	22.2	COLD	WEAK	N C	DIFFUSE
AUG 13	13	COSHOCTON	S	1.9	STAT	WEAK	N C	DIFFUSE
AUG 14	3	COSHOCTON	N	0.9	STAT	WEAK	N C	DIFFUSE
AUG 14	12	COSHOCTON	S	1.4	STAT	WEAK	N C	DIFFUSE
AUG 14	13	COSHOCTON	N	1.4	STAT	WEAK	N C	DIFFUSE
AUG 14	17	COSHOCTON	S	3.0	STAT	WEAK	N C	DIFFUSE

Table 2 (continued).

DATE	HR	LOCATION	DIR	SP	TYPE	INTENSITY		CHARACTER
AUG 15	0	COSHOCTON	W	14.8	COLD	WEAK	N C	DIFFUSE
AUG 15	2	MC HENRY	W	7.9	COLD	WEAK	N C	DIFFUSE
AUG 15	3	LEWISBURG	NW	6.2	COLD	WEAK	N C	DIFFUSE
AUG 20	15	COSHOCTON	NW	8.8	COLD	WEAK	N C	WITH WAVES
AUG 20	21	KANE	W	10.4	COLD	WEAK	N C	WITH WAVES
AUG 20	21	MC HENRY	NW	13.9	COLD	WEAK	N C	WITH WAVES
AUG 21	0	LEWISBURG	NW	8.3	COLD	WEAK	N C	WITH WAVES
AUG 21	3	KANE	E	9.3	COLD	WEAK	N C	WITH WAVES
AUG 21	2	MC HENRY	SW	13.4	COLD	WEAK	N C	WITH WAVES
AUG 21	1	LEWISBURG	SW	6.9	COLD	WEAK	N C	WITH WAVES
AUG 21	6	KANE	N	1.6	COLD	WEAK	N C	WITH WAVES
AUG 21	10	MC HENRY	W	14.8	COLD	WEAK	N C	WITH WAVES
AUG 21	10	LEWISBURG	NW	20.4	COLD	WEAK	N C	WITH WAVES
SEP 5	21	COSHOCTON	NW	13.2	COLD	WEAK	N C	DIFFUSE
SEP 6	11	KANE	NW	12.0	COLD	WEAK	N C	DIFFUSE
SEP 6	22	MC HENRY	NW	6.0	COLD	WEAK	N C	DIFFUSE
SEP 7	5	LEWISBURG	NW	14.4	COLD	WEAK	N C	DIFFUSE
SEP 6	8	COSHOCTON	SW	9.3	COLD	WEAK	N C	QUASI-STATIONARY
SEP 6	10	COSHOCTON	NW	13.0	COLD	WEAK	N C	DIFFUSE
SEP 11	19	COSHOCTON	NW	11.6	COLD	WEAK	N C	WITH WAVES
SEP 11	19	KANE	NW	11.8	COLD	WEAK	N C	WITH WAVES
SEP 12	2	MC HENRY	N	4.4	COLD	WEAK	N C	DIFFUSE
SEP 12	12	LEWISBURG	N	7.4	COLD	WEAK	N C	DIFFUSE
SEP 16	4	COSHOCTON	N	9.7	COLD	MOD	N C	WITH WAVES
SEP 16	4	KANE	NW	9.5	COLD	MOD	N C	WITH WAVES
SEP 16	16	MC HENRY	NW	5.8	COLD	WEAK	N C	WITH WAVES
SEP 17	9	LEWISBURG	N	3.5	COLD	WEAK	N C	WITH WAVES
SEP 17	22	COSHOCTON	SW	5.6	WARM	WEAK	N C	DIFFUSE
SEP 17	16	LEWISBURG	SW	2.3	WARM	WEAK	N C	
SEP 18	7	KANE	W	6.9	OCCL	WEAK	N C	
SEP 18	8	MC HENRY	NW	11.1	COLD	WEAK	N C	
SEP 18	12	LEWISBURG	NW	5.3	COLD	WEAK	N C	DIFFUSE
SEP 20	16	COSHOCTON	NW	9.7	COLD	WEAK	N C	
SEP 20	16	KANE	NW	10.2	STAT	MOD	DECR	ACTIVITY UNCHANGED
SEP 22	11	COSHOCTON	SW	30.1	WARM	WEAK	N C	DIFFUSE
SEP 22	14	KANE	W	19.4	WARM	WEAK	N C	
SEP 23	3	COSHOCTON	NW	6.0	COLD	WEAK	N C	WITH WAVES
SEP 24	1	MC HENRY	N	3.7	STAT	WEAK	N C	WITH WAVES
SEP 24	10	LEWISBURG	W	13.9	COLD	WEAK	DECR	DIFFUSE
SEP 23	23	COSHOCTON	N	7.6	COLD	WEAK	N C	DIFFUSE
SEP 23	23	KANE	NW	8.8	COLD	WEAK	N C	DIFFUSE
SEP 26	22	COSHOCTON	N	2.5	STAT	WEAK	N C	WITH WAVES
SEP 26	6	KANE	N	6.0	COLD	WEAK	N C	
SEP 29	23	MC HENRY	N	10.9	COLD	WEAK	N C	
30	10	LEWISBURG	NE	5.6	COLD	WEAK	N C	
SEP 29	2	COSHOCTON	S	3.2	STAT	WEAK	N C	WITH WAVES
SEP 29	4	COSHOCTON	N	3.2	STAT	WEAK	N C	DIFFUSE
SEP 29	7	COSHOCTON	S	6.5	STAT	WEAK	N C	DIFFUSE
SEP 29	16	COSHOCTON	N	5.1	STAT	WEAK	N C	DIFFUSE
SEP 29	22	KANE	N	15.3	COLD	WEAK	N C	

the frontal systems were classified as weak, with generally decreasing or unchanged intensity.

4.3 Characteristics of Pressure Systems

Pressure systems can be characterized in several ways: The intensity of the pressure system, i.e., the magnitude of the departure of the central pressure from standard conditions; the pressure gradient, i.e., the rate of change of pressure with distance; the areal coverage; and finally, the rate of movement of the pressure system. An analysis of the areal extent of several high pressure systems during August and September was attempted. The area enclosed by the 1020-mb isobar and the magnitude of the central pressure were recorded at twelve-hour intervals. The ratio of the maximum pressure less 1020-mb to the area enclosed by the 1020-mb isobar served as a measure of the pressure system intensity. The areal coverage varied greatly from analysis to analysis. The ratio showed no relationship to the ozone concentrations at McHenry. Attempts to recognize a relationship between the intensity of central pressure or the areal coverage with ozone concentration appeared fruitless and further research was abandoned.

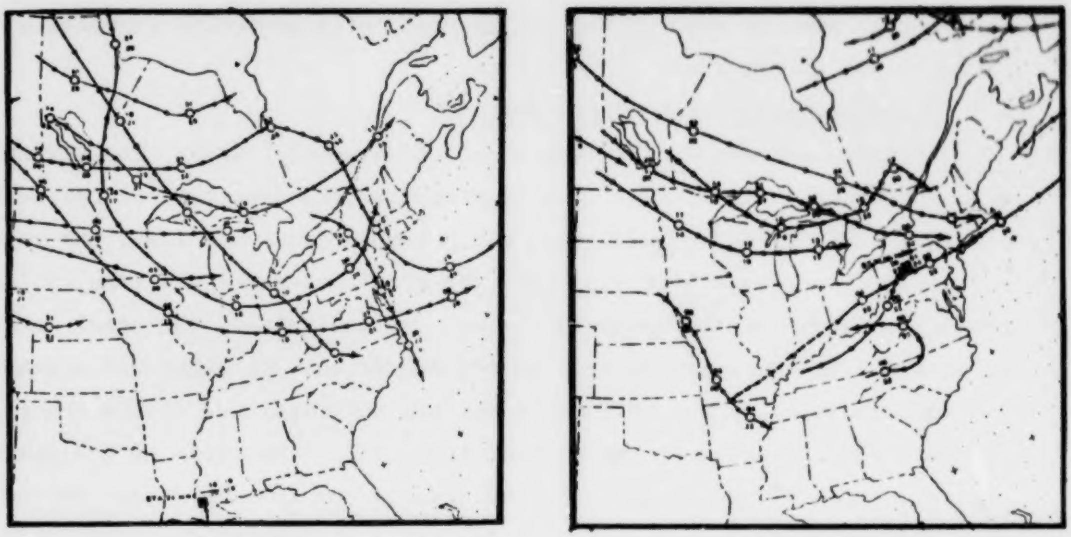
The movement of high pressure systems during the four-month period are presented in Figure 3. Fronts occasionally crossed the study area. The low pressure centers associated with fronts passed generally west and north of the study area leaving only the high pressure systems to penetrate onto the study area.

4.4 Ozone Concentrations and Thunderstorms

Twelve-hour average ozone concentrations at McHenry were examined for those days when thunder was reported at Pittsburgh and compared with the previous and following day's concentration. (Pittsburgh was the nearest National Weather Service office reporting thunder in its LCD). Usually, concentrations decreased following the thunder. At the time scale investigated, no particular relationship of the two quantities was found.

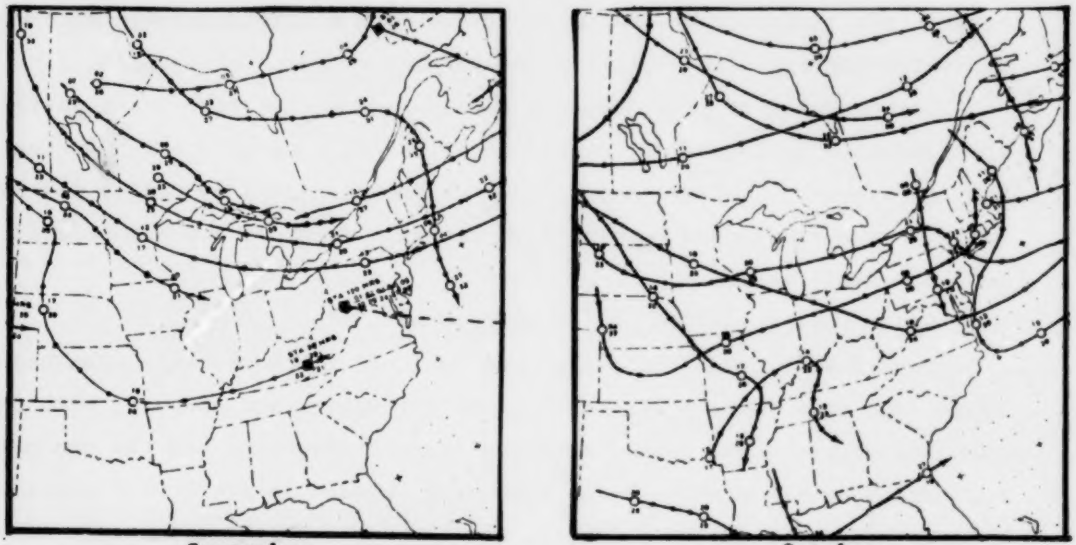
4.5 Ozone Concentrations and Sky Cover

Several measures of cloudiness--daytime cloud cover, percent of possible sunshine, and the hours of sunshine--were plotted for July through September from the Pittsburgh LCD. In comparing those plots to the twelve-hour average ozone concentration at McHenry, no consistent common trends of the data sets were noted. This result does not suggest that



July

August



September

October

Circle indicates position of center at 7:00 a.m. E.S.T. Figure above circle indicates date, figure below, pressure to nearest millibar. Dots indicate intervening 6-hourly positions. Squares indicate position of stationary center for period shown. Dashed line in track indicates reformation at new position. Only those centers which could be identified for 24 hours or more are included.

Figure 3. Tracks of centers of high pressure systems at sea level, by months, 1973. (Source: Climatological Data, National Summary, 24, 7-10, Environmental Data Service, Asheville, N.C.)

sunlight, especially in the ultraviolet portion, has no effect on ozone concentrations. The reported variables are not good indicators of the light intensity, wavelength or amount.

4.6 Time-Section Analyses

4.6.1 Potential Temperature

A common technique used to analyze the vertical structure of the atmosphere as a function of time is the vertical time section. It is advantageous in such studies to examine conservative properties in order to diagnose the ongoing processes. The potential temperature, θ, given by the equation

$$\theta = T\left(\frac{1000}{P}\right)^{R/C_p}$$

where T is the temperature (K),

P is the pressure (mb),

R is gas constant for dry air, and

C_p is the specific heat at constant pressure for dry air ($R/C_p = 2/7$).

In adiabatic processes, θ is conserved. Its distribution indicates the warm or cold conditions. When the vertical gradient of θ, $\frac{\partial\theta}{\partial z}$, is large, the air is quite stable. As $\frac{\partial\theta}{\partial z}$ decreases, the air tends toward instability. The time section of θ show these changes. Since θ is conserved in adiabatic processes, downward movement of a θ isopleth from one observation to another indicates descending motion, and/or warm air advection. A basic discussion of the use of θ as an analysis variable is given in Appendix A.

4.6.2 Dewpoint Depression

A measure, although not conservative, of the amount of moisture within the air, is the difference between the existing temperature and the dewpoint temperature. When the depression is small ($\leq$ 3°C), the air is nearly saturated. When the separation is large (> 15°C), the air is quite dry. The altitudes of these moist and dry conditions were computed for each rawinsonde sounding.

4.6.3 Significant Temperature Layers

A third characteristic in time-section analyses is the presence or absence of temperature inversions; i.e., layers in which air temperature increases with altitude. Inversions are layers of stable air, resisting transfer of momentum and mass across their boundaries. Aloft, they often mark a boundary between types of air. Those inversions which persist, indicate that the contrast across them is maintained. Their presence also indicates the potential for trapping ground-based emissions and increasing concentrations. Lowering the altitude of the inversion, decreases the dispersion volume, leading to high pollutant concentrations. The longer the inversion persists, the greater the opportunity for degrading the local air quality. Therefore, the altitude, motion or persistence of the inversion layer, are documented and examined in relation to ozone concentration. Surface-based inversions often develop during the night due to radiative heat loss at the ground. These are quickly dissipated by solar heating on the next day and are not considered in analyses which are presented.

Superadiabatic layers, i.e., those layers where the temperature decreases at a rate greater than 9.8°C km^{-1} (the adiabatic lapse rate) are ideal layers for transferring momentum and mass from one altitude to another. These layers are common near the ground on a hot summer afternoon, but are infrequently found aloft and seldom persist for any length of time because of their unstable characteristics. The reader is referred to the discussions of Appendix A.

4.6.4 Computations and Presentation of Results

The vertical time-sections of potential temperature, θ, dewpoint depression and significant temperature layers were computed for Pittsburgh, Buffalo, Huntington, and Dayton for each sounding from July 1 to October 31. The analyses were drawn from computer printouts of data at 100-meter increments in the vertical after each sounding was analyzed independently of all the others. The analyses of the time-sections of θ and of temperature inversions that could be identified in two consecutive rawinsonde observations are presented in Figure 4. Cross-sections of the dewpoint depression were plotted in a similar manner, but are not given here. The time and type of frontal passage at each ozone monitoring location and a plot of the twelve-hour average ozone concentrations are shown on the upper portion of Figure 4 so all of these data can be examined concurrently.

4.7 Data Interpretation

The plots, by month, of the ozone concentration at each of the four observing stations indicate that Lewisburg and Coshocton normally exhibit a fairly strong diurnal trend, i.e., high concentrations with the 0000 GMT

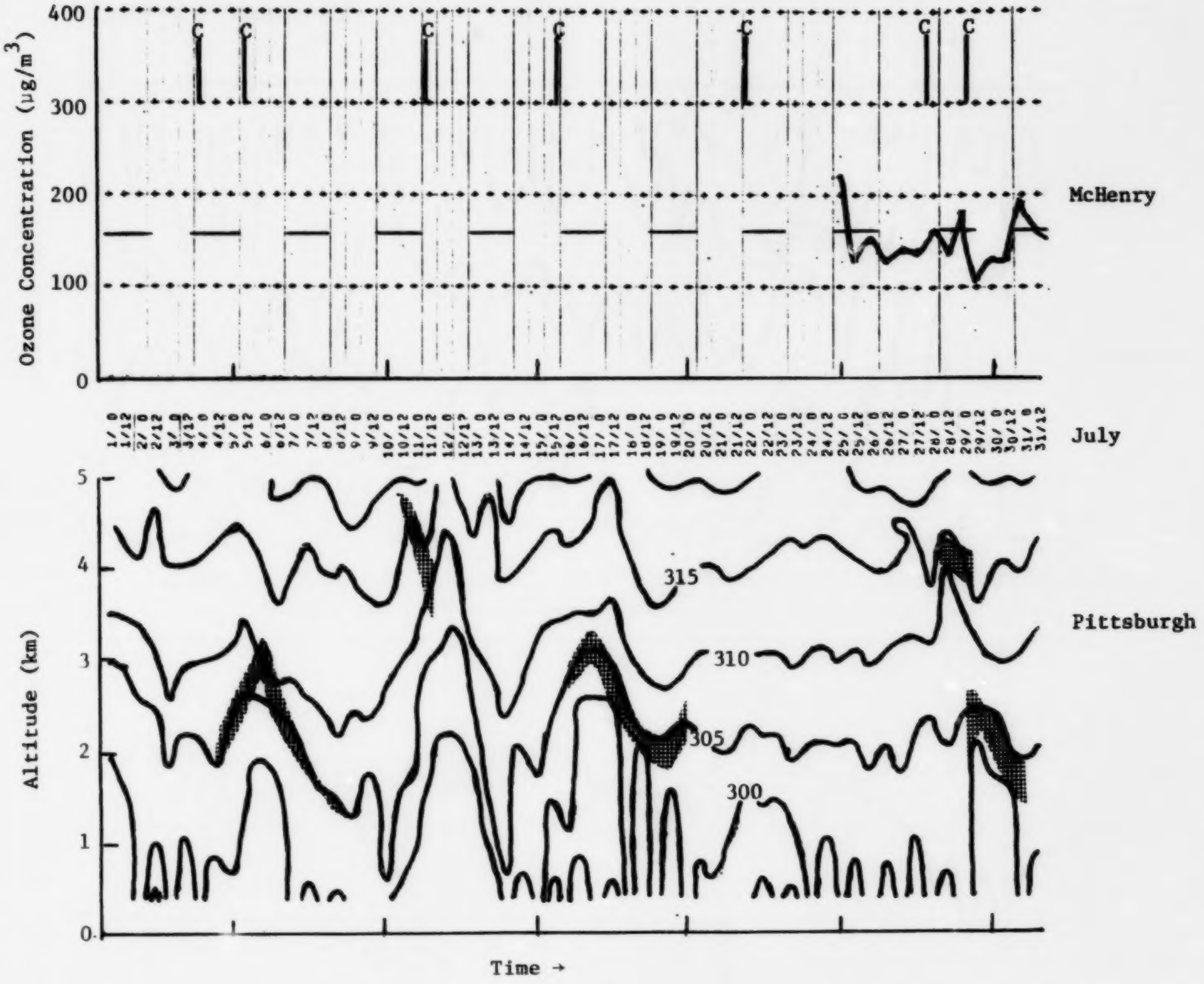
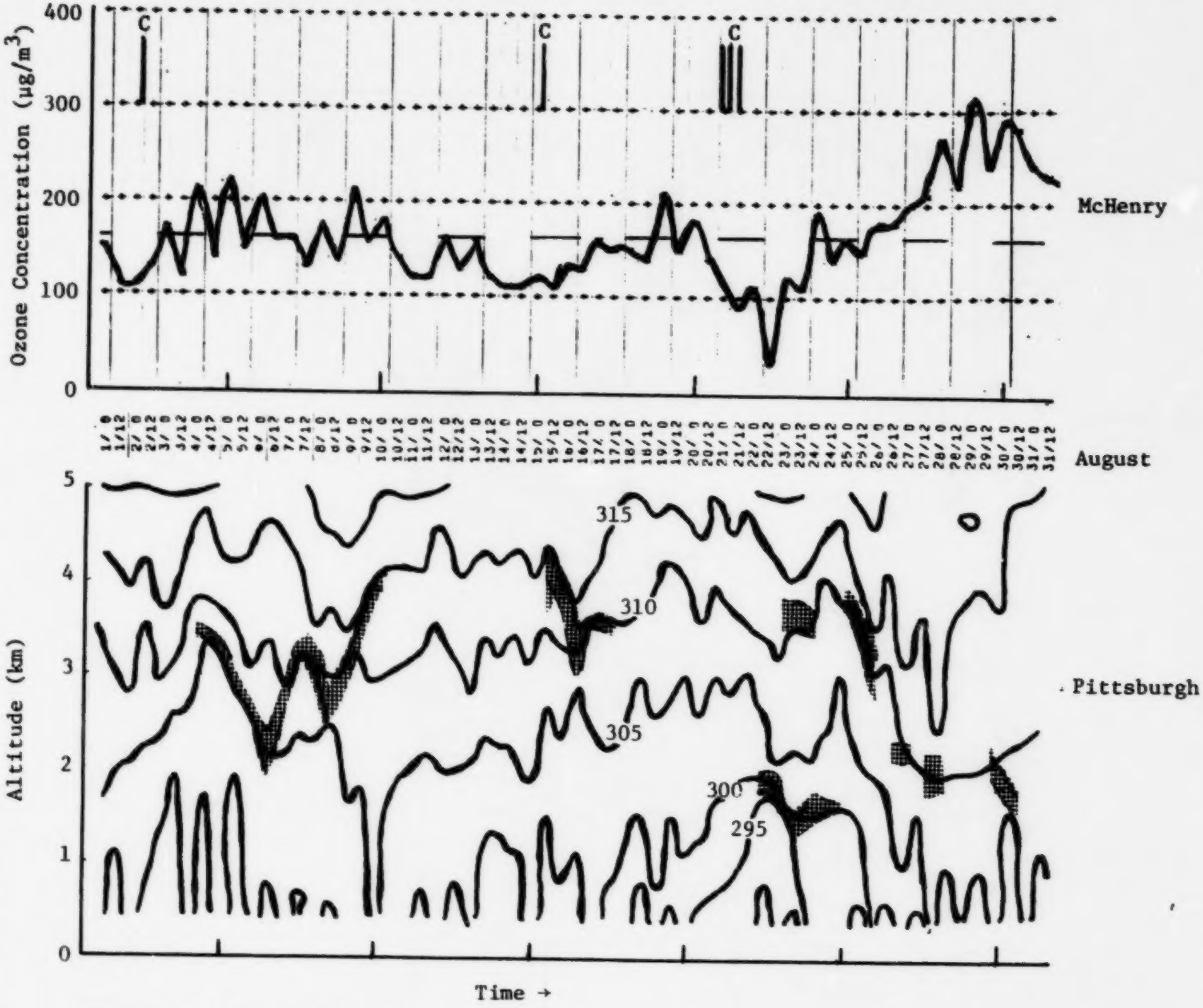


Figure 4. Average ozone concentration and vertical potential temperature distribution at twelve-hour intervals at the indicated locations for the given month. Date, time, and type of frontal passages are also indicated. Stippled regions indicate inversions aloft.



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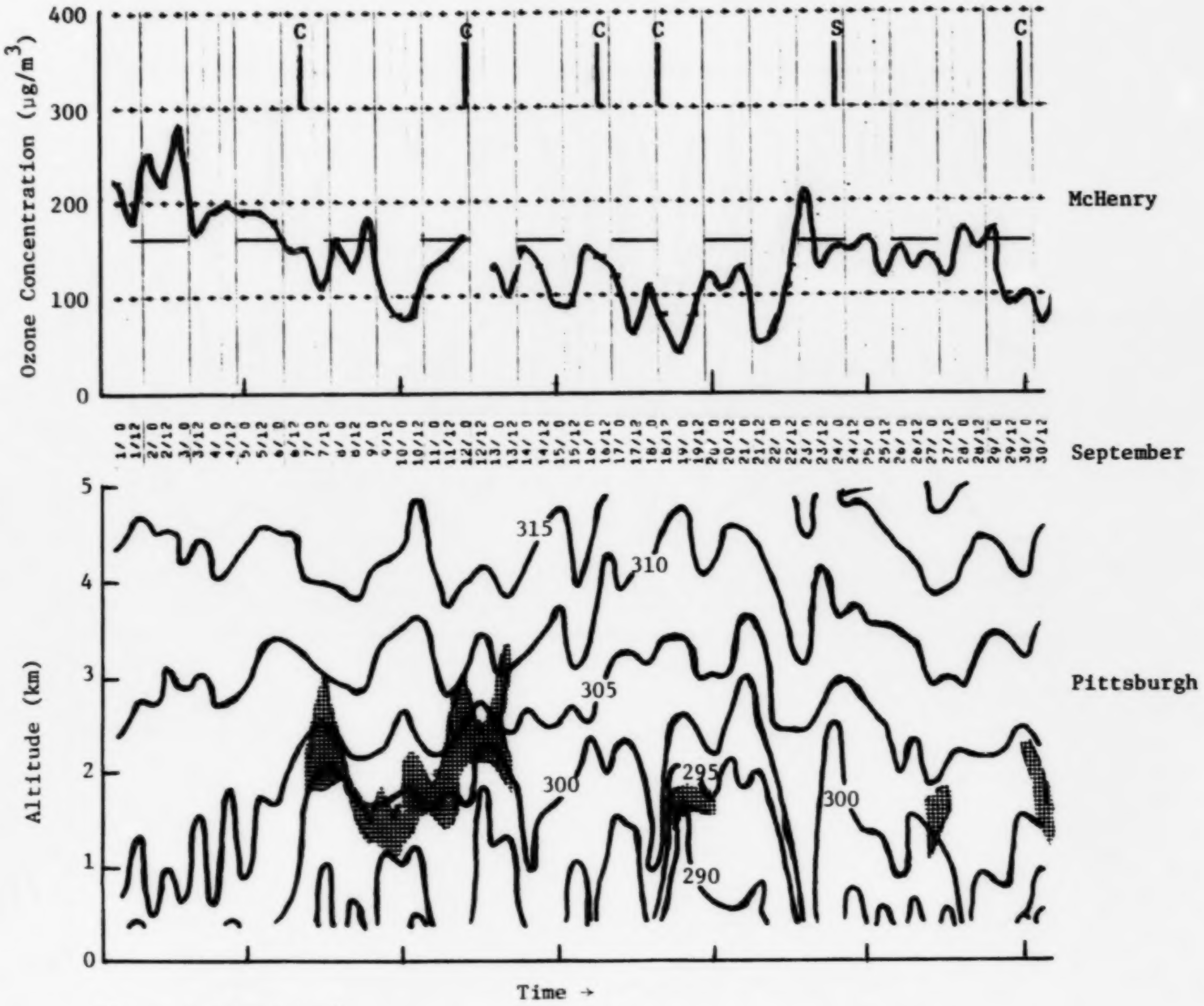

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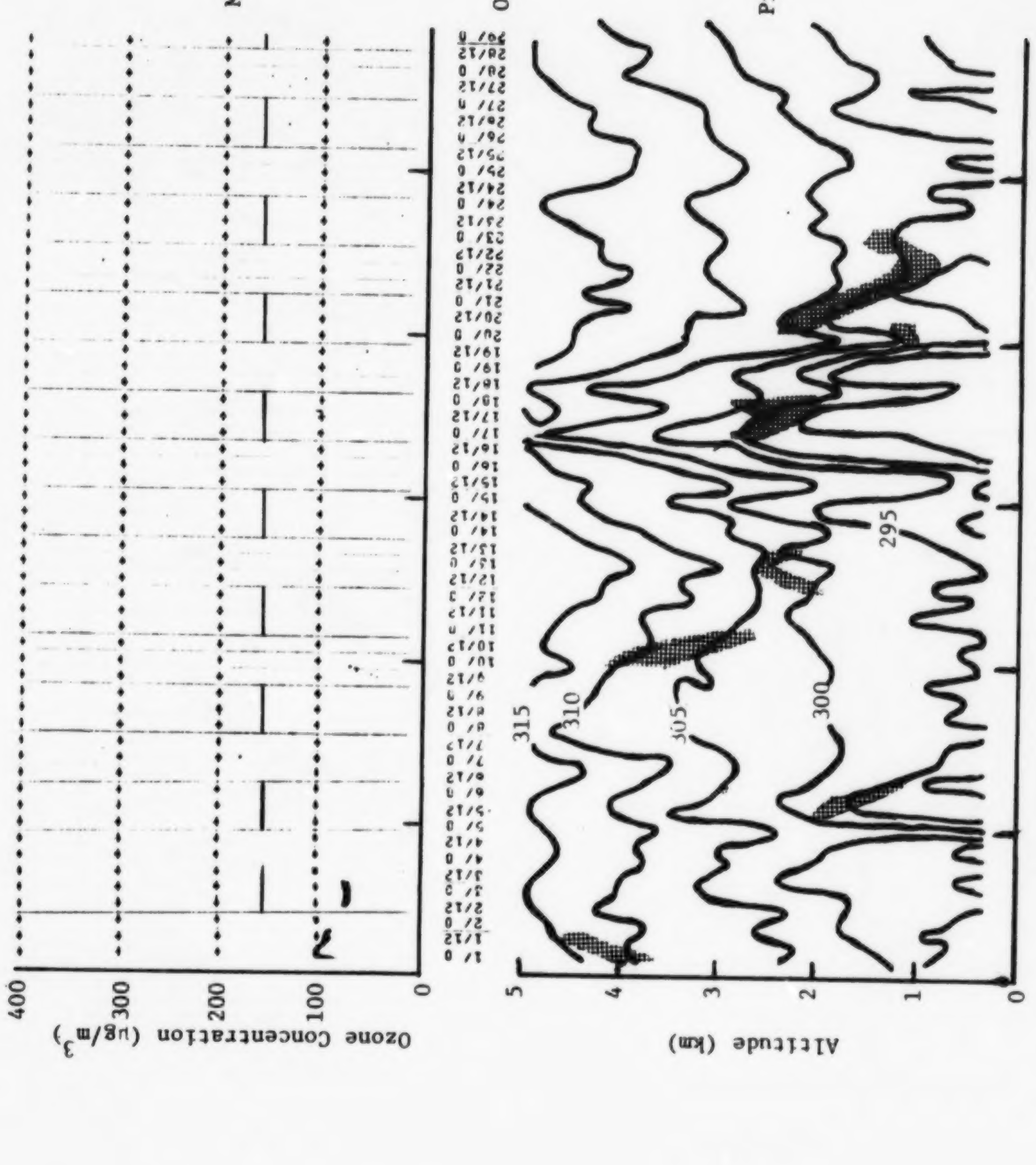

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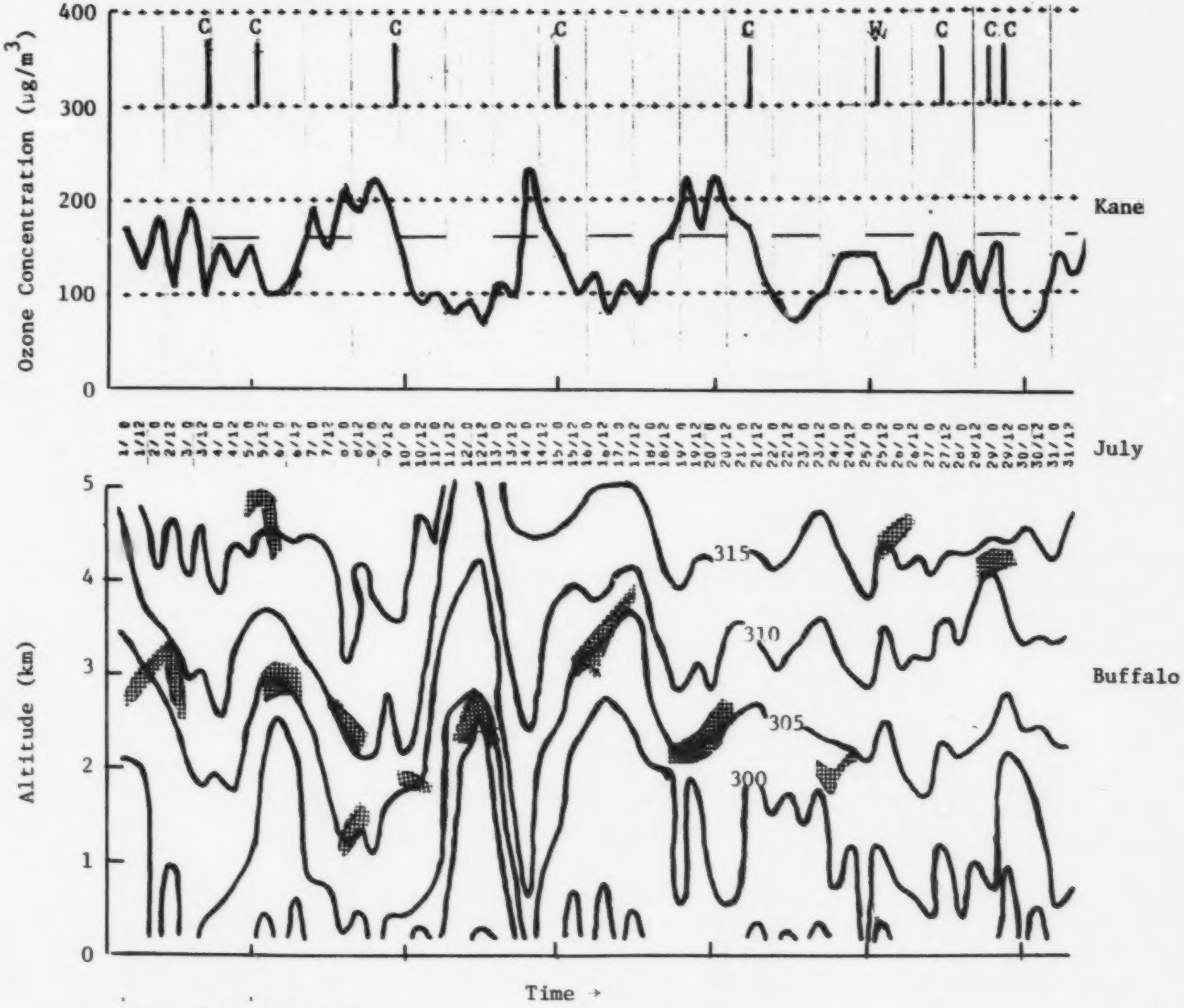

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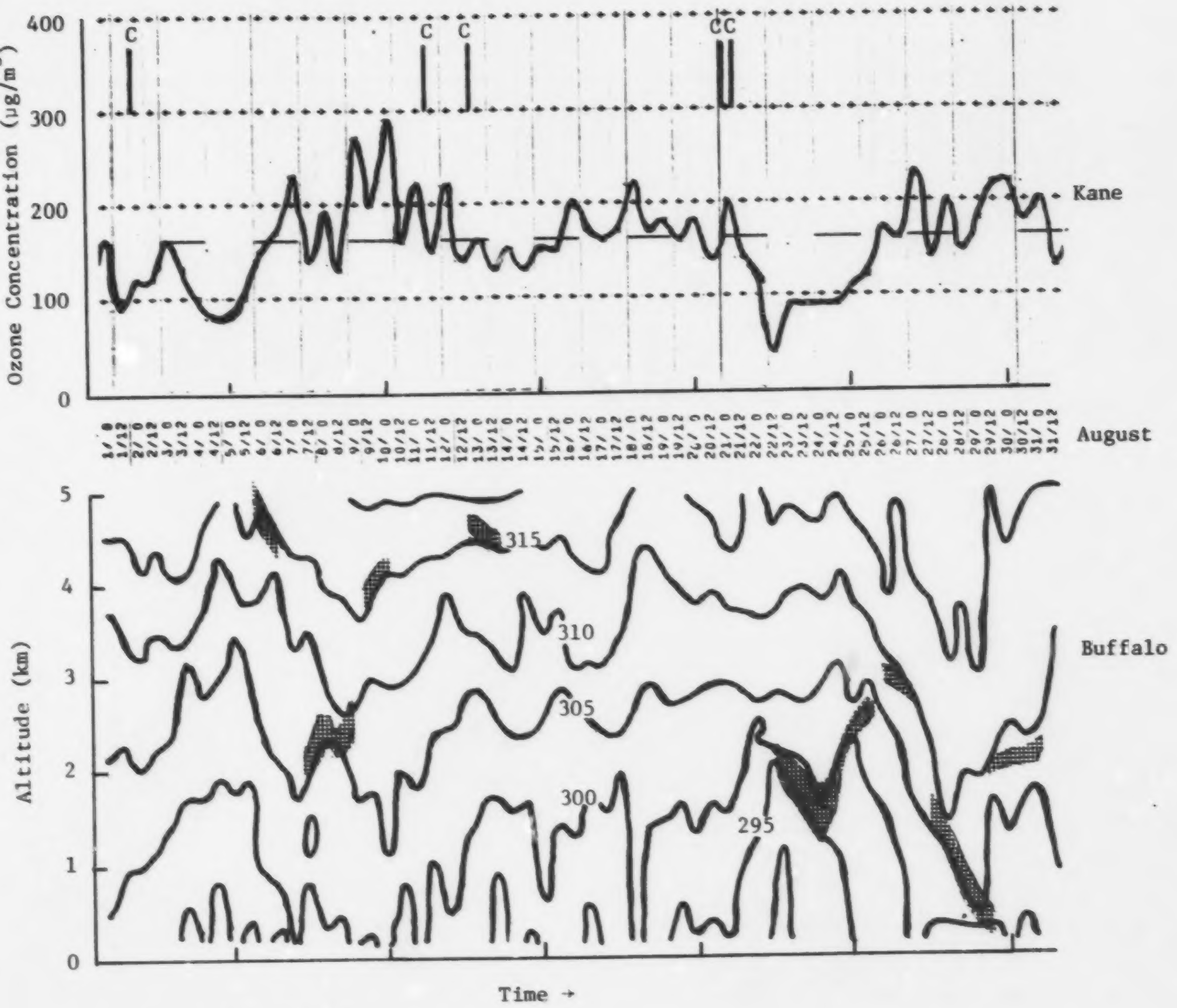

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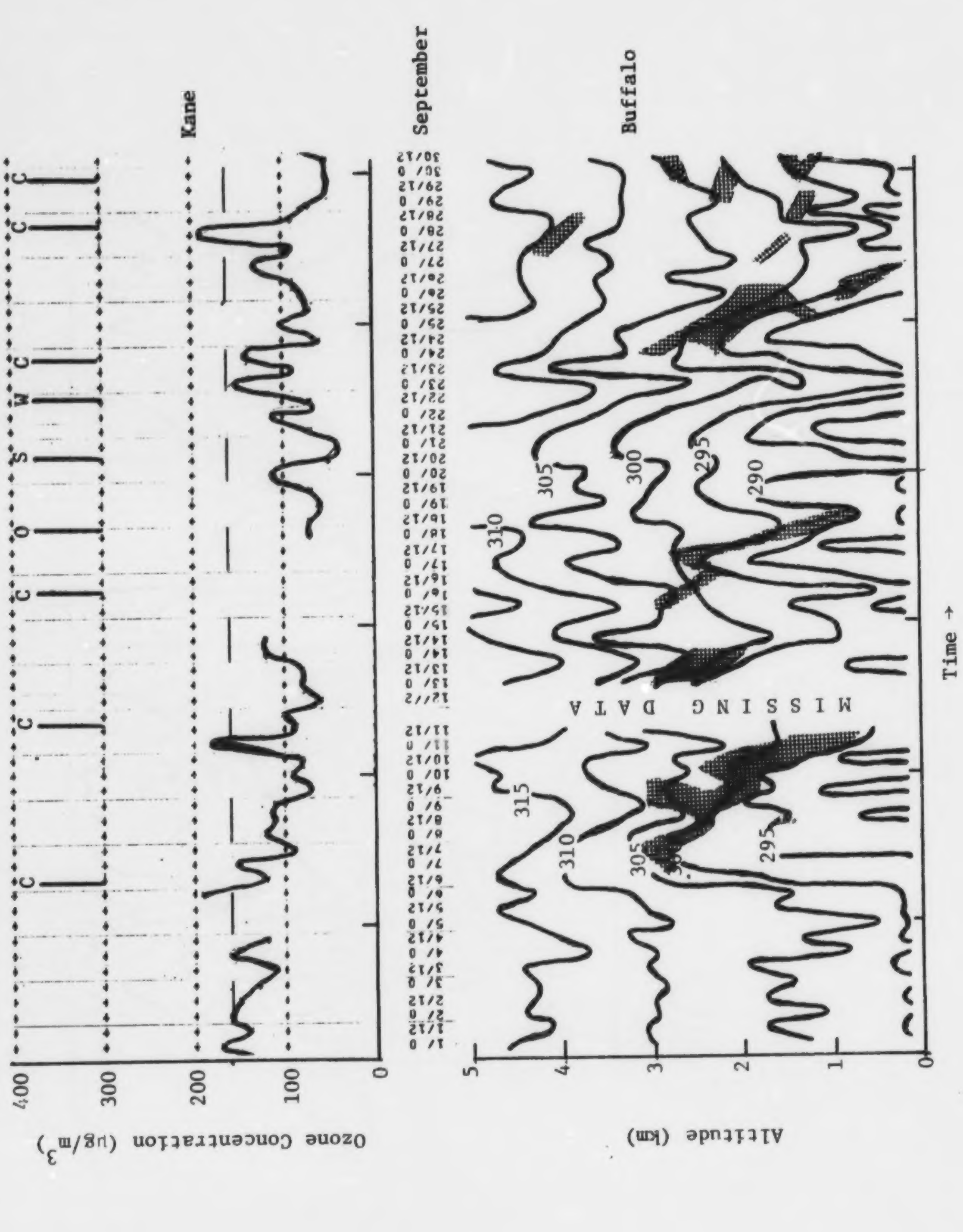

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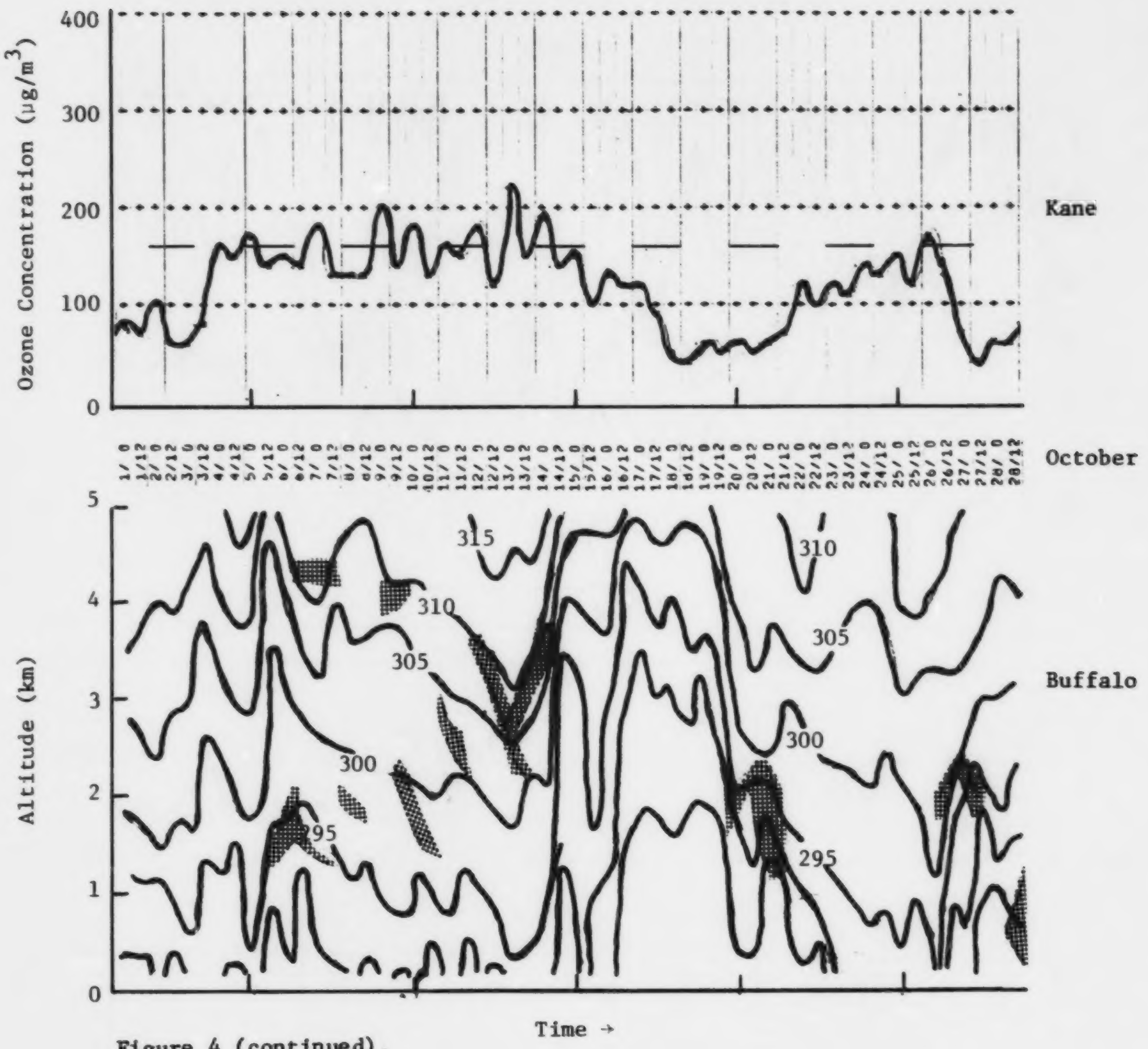

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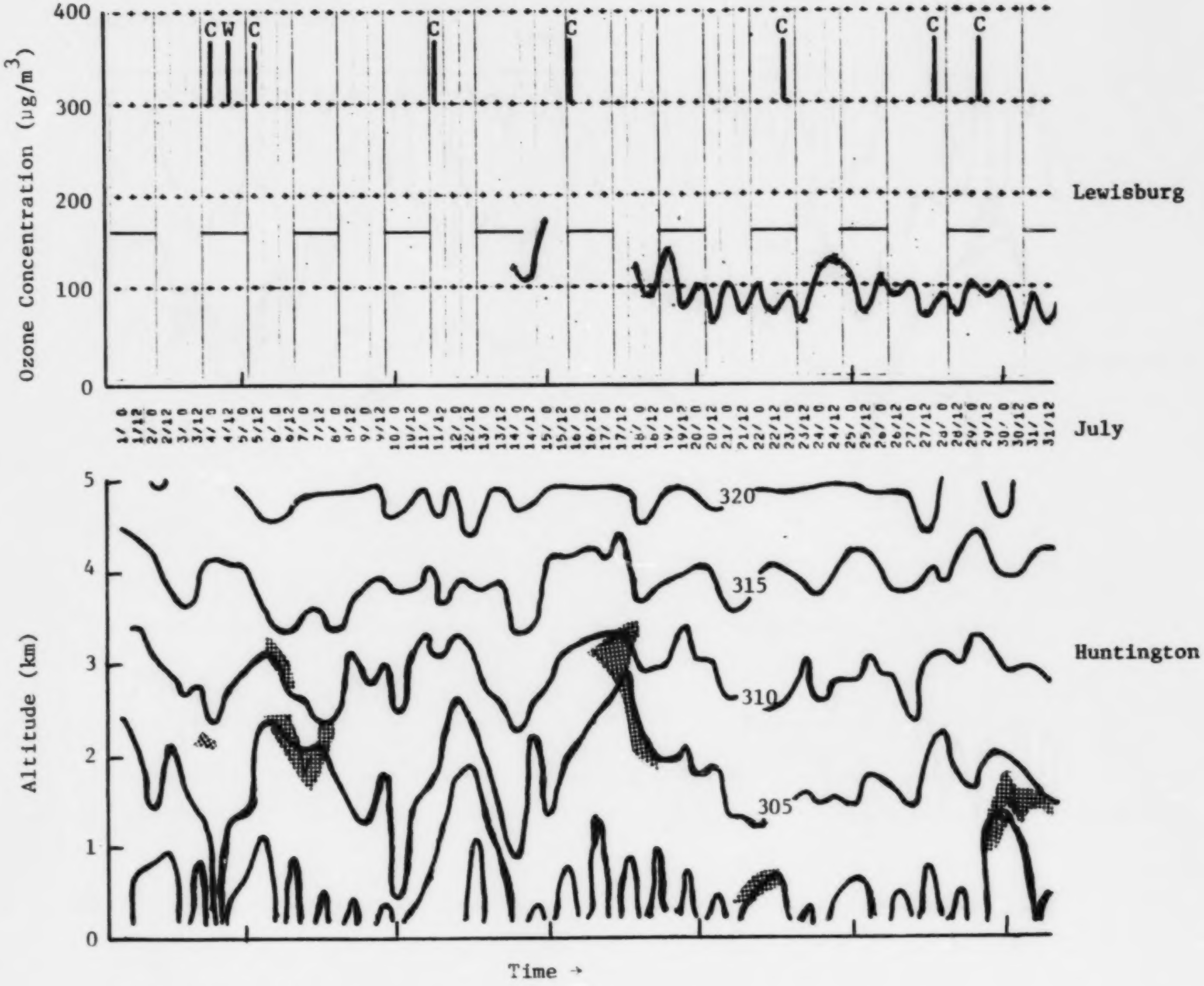

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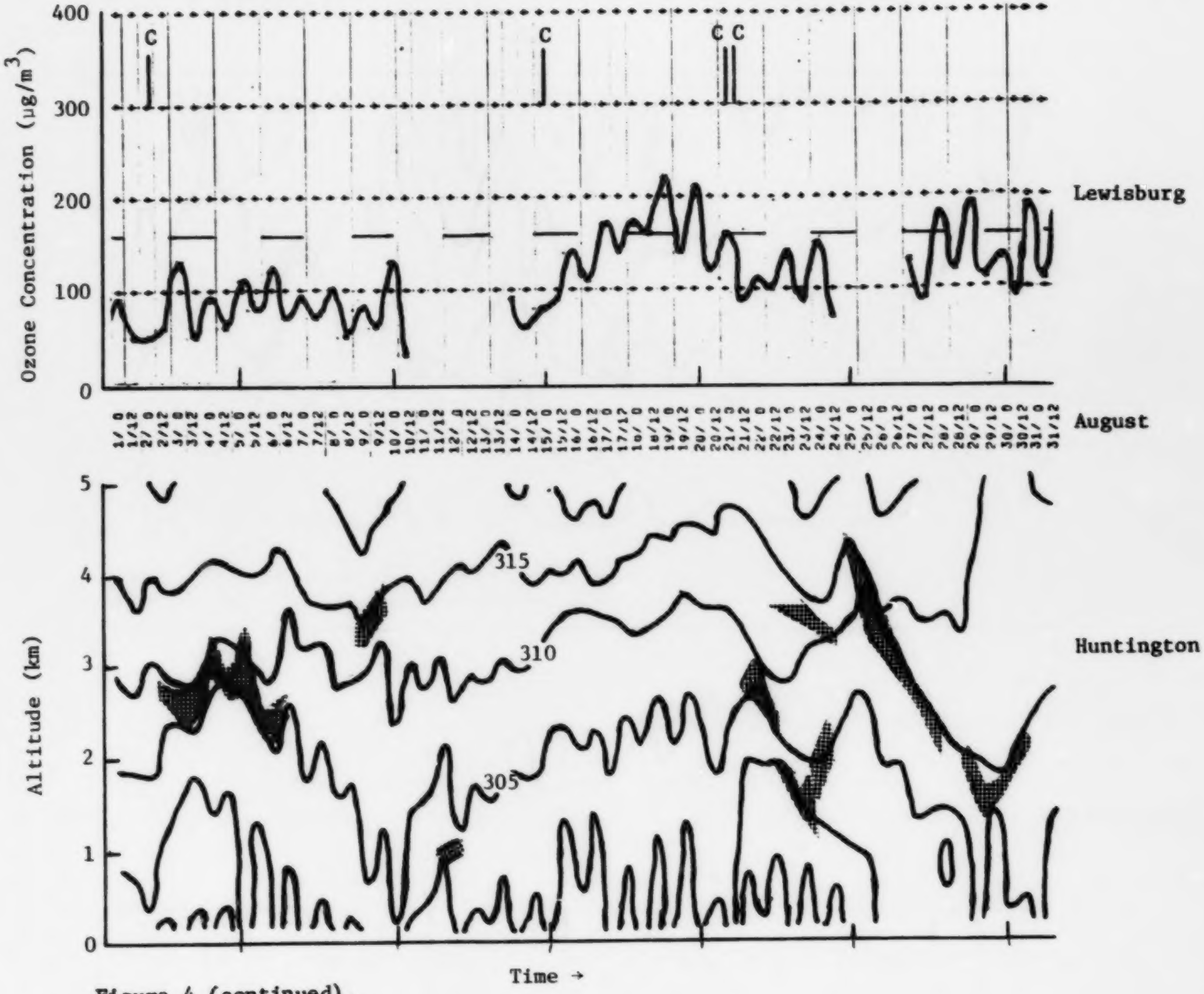

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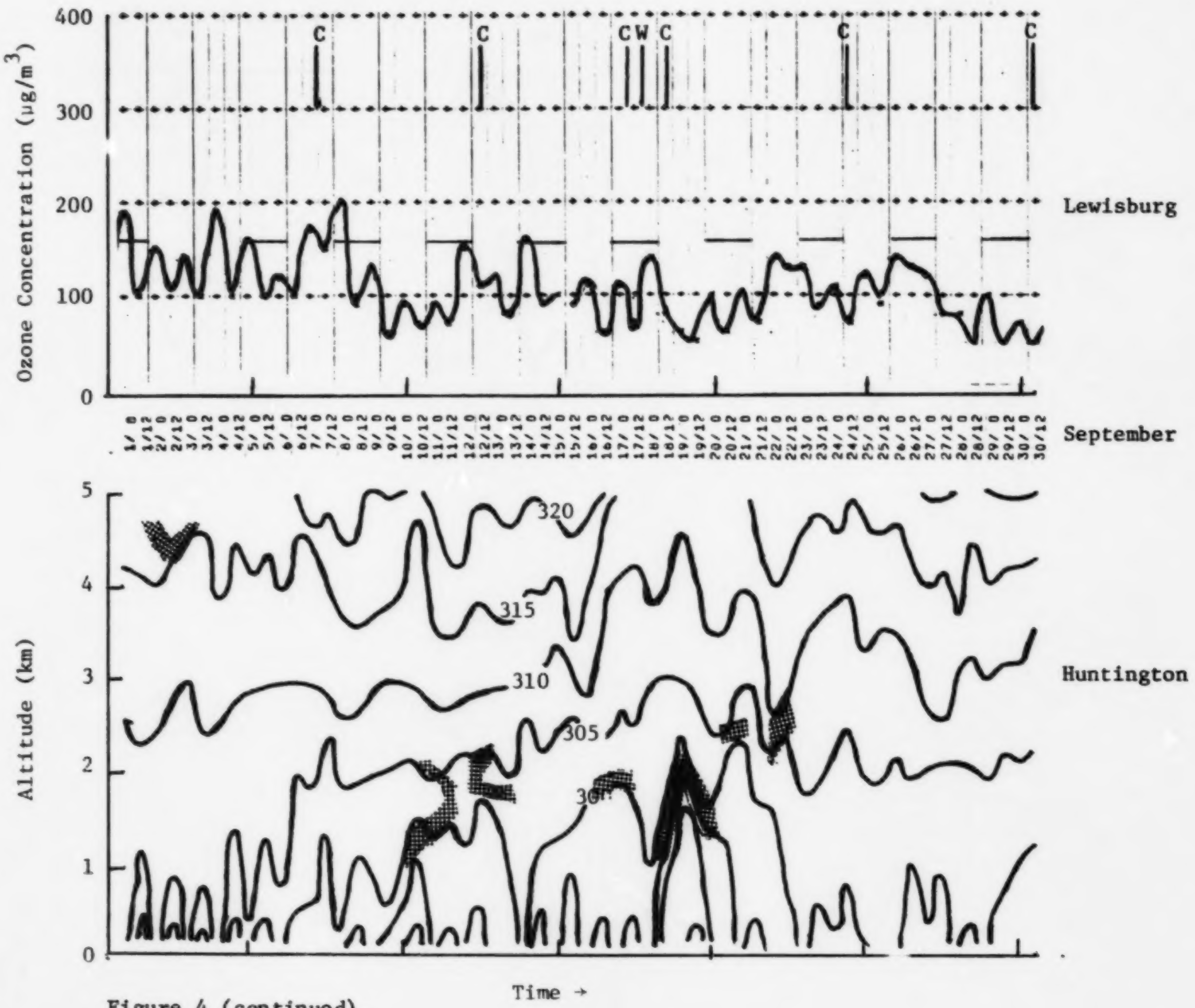

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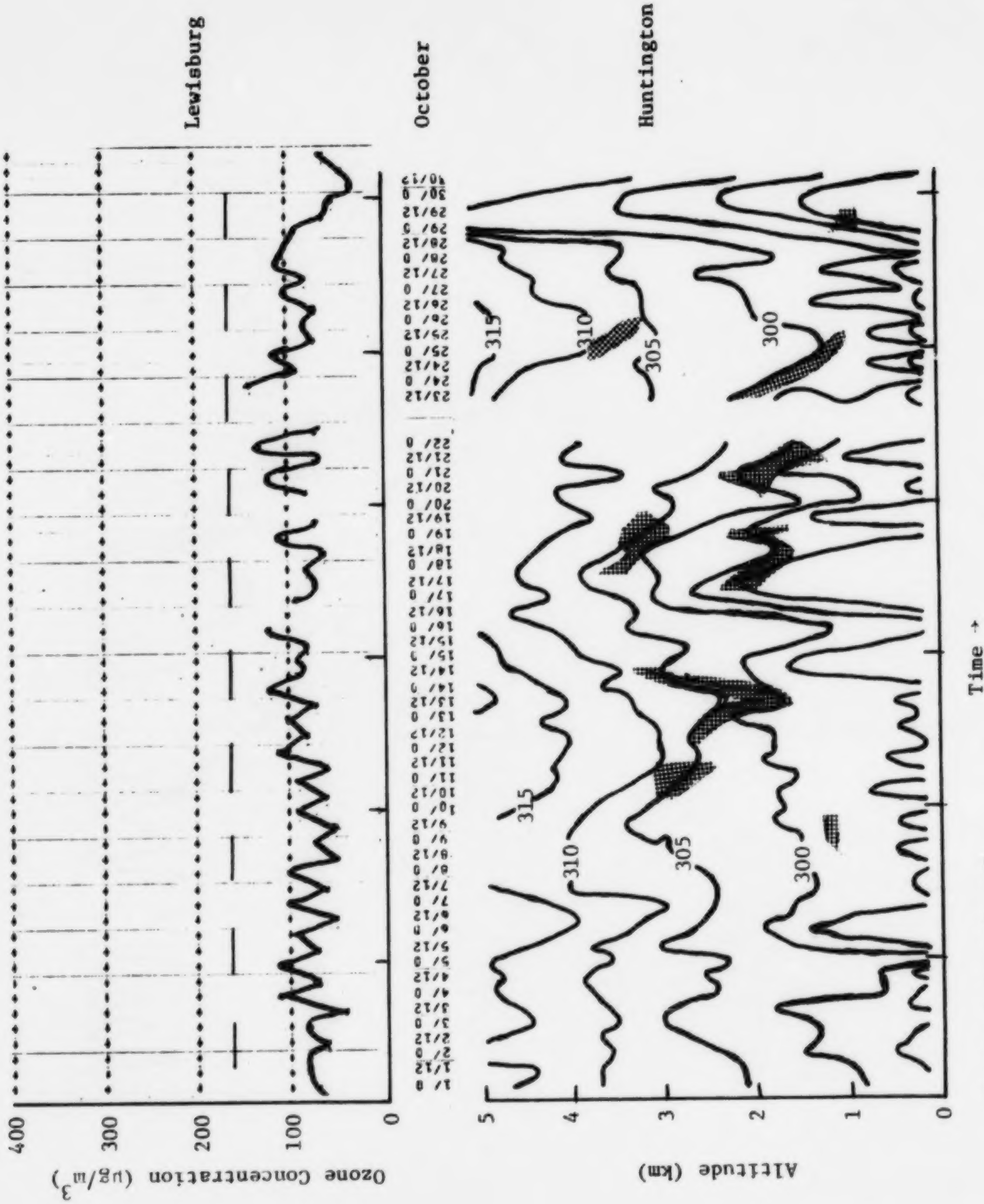

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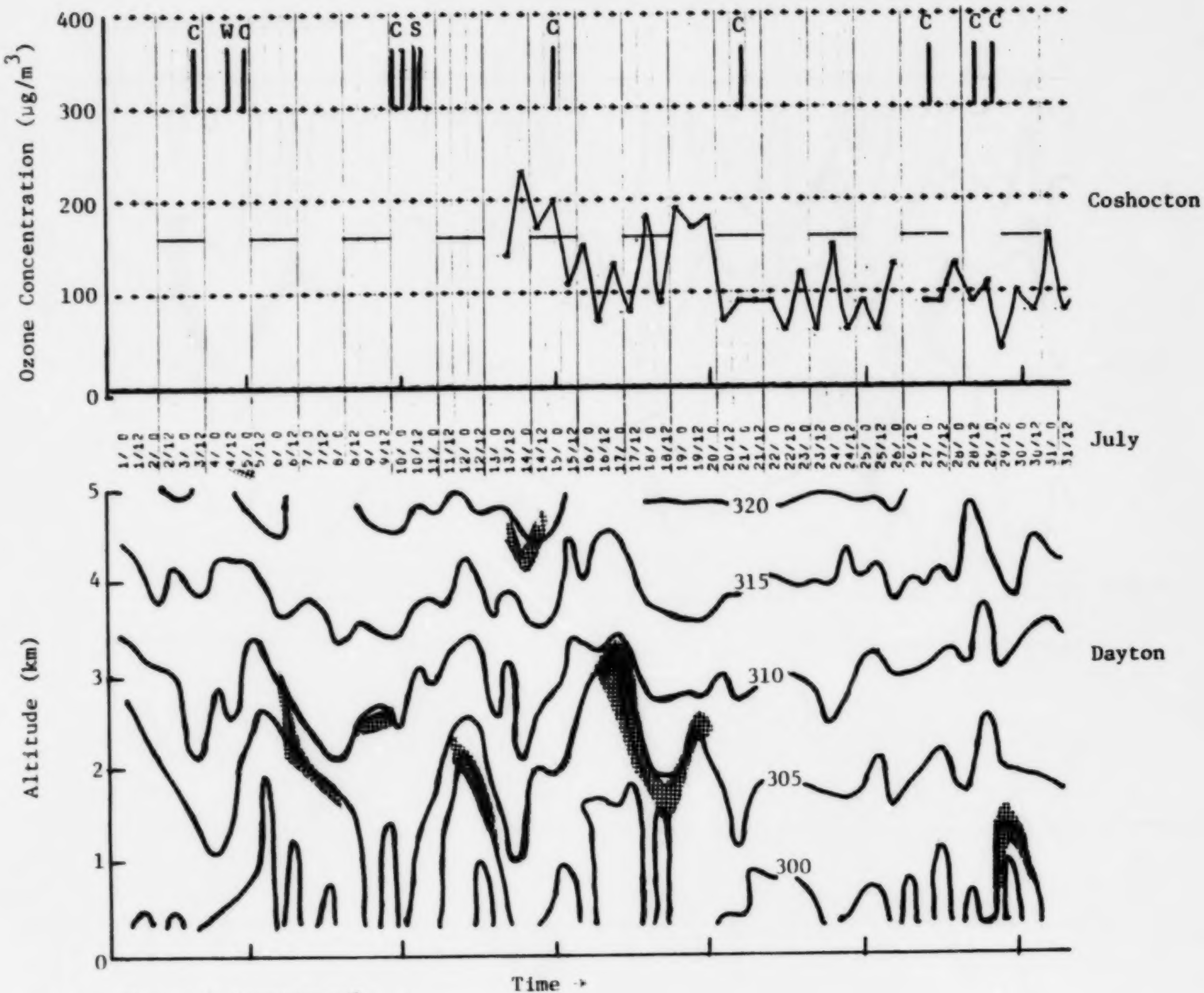

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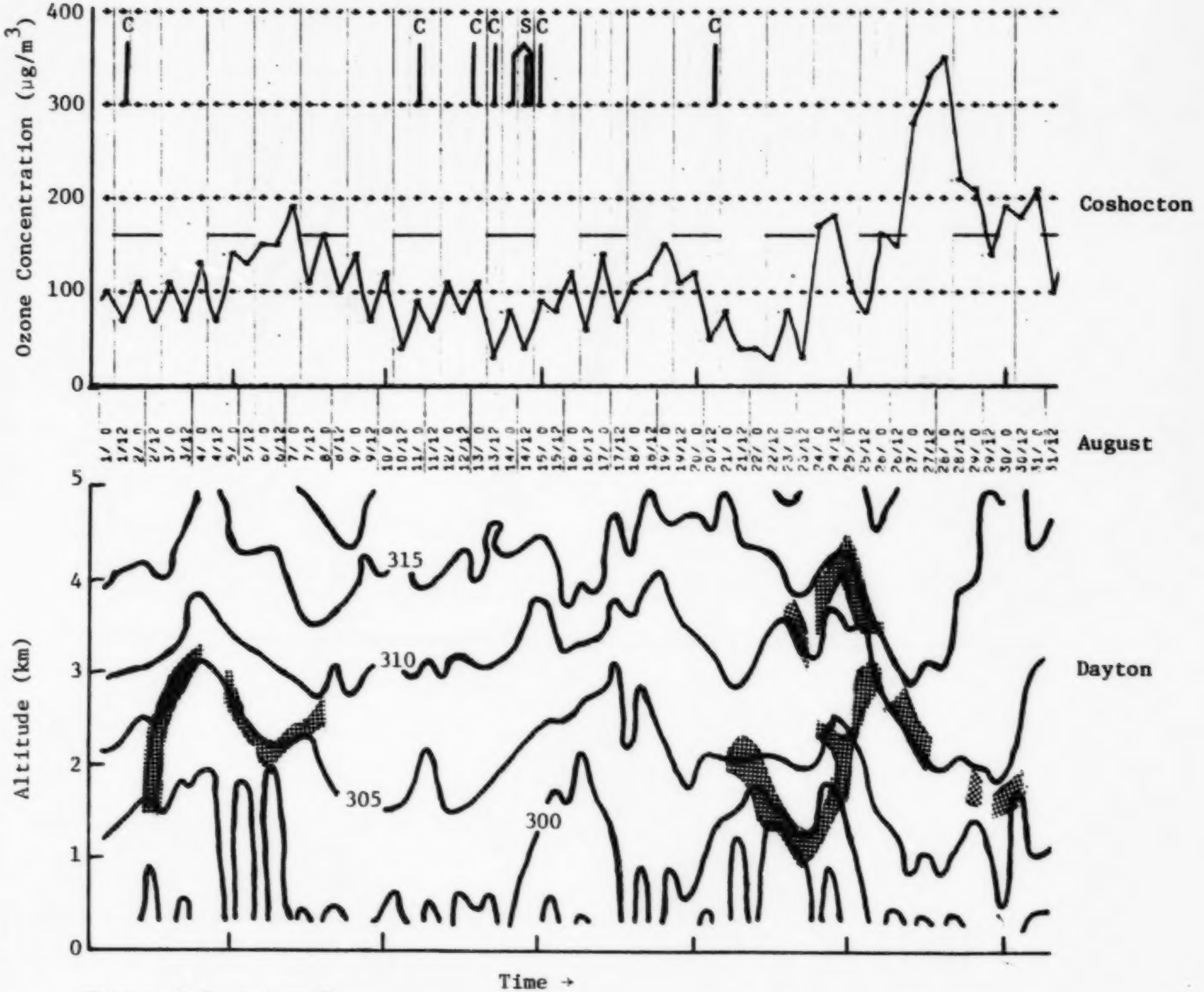

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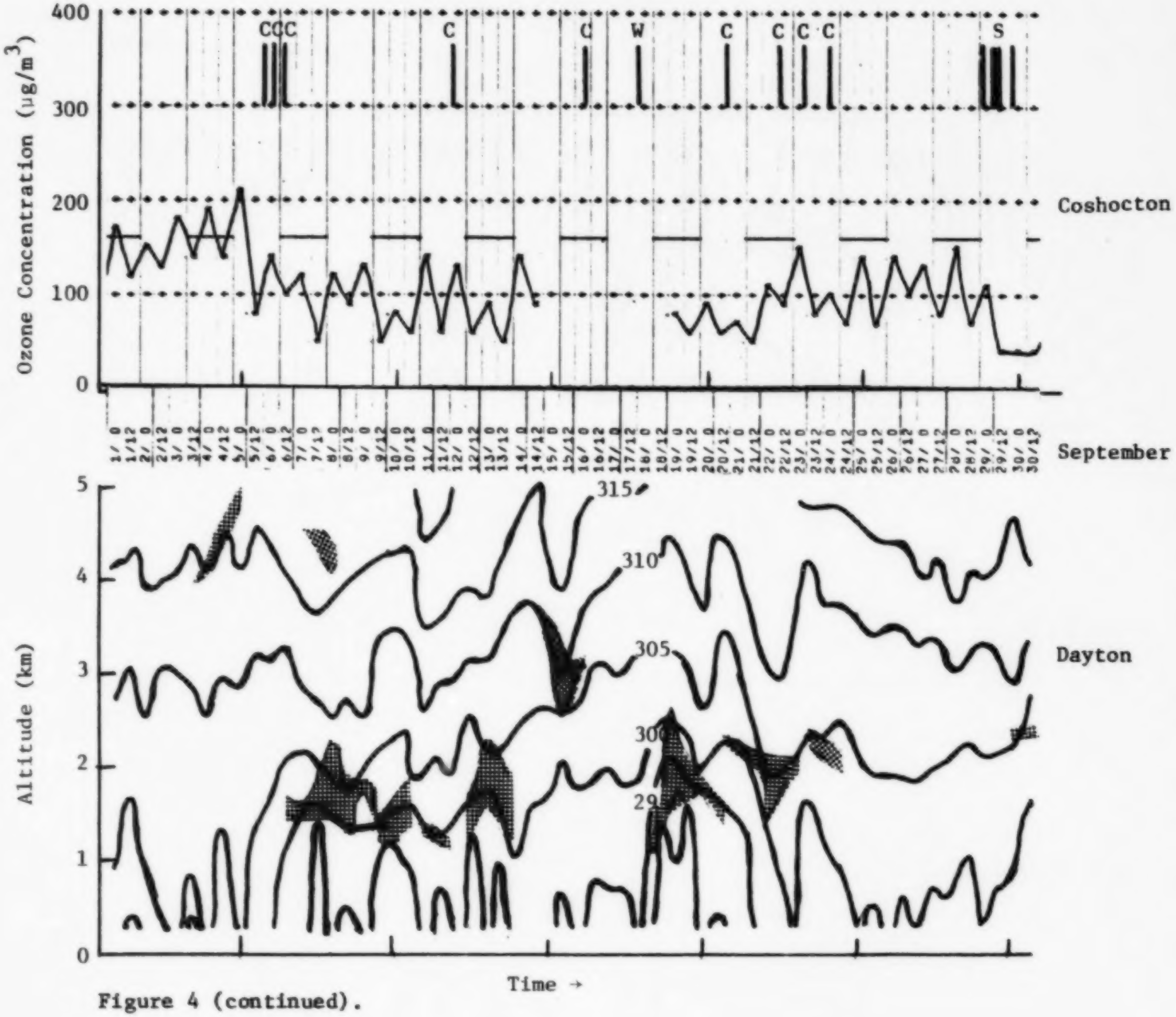

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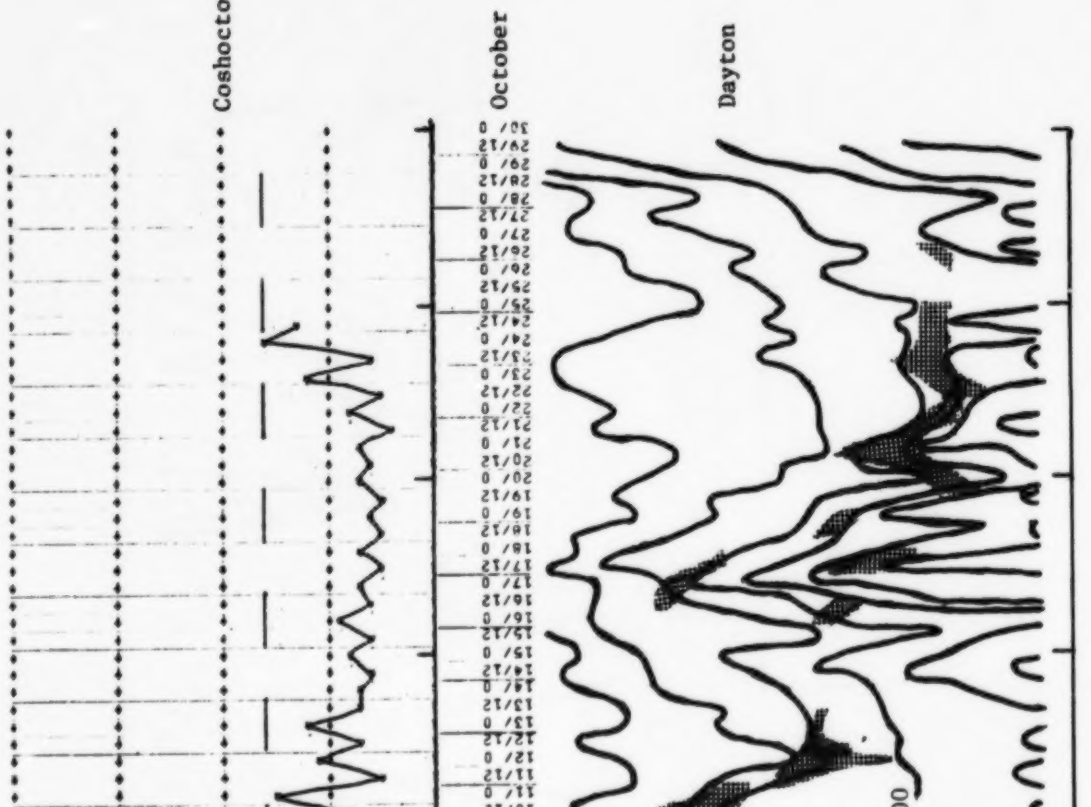


Figure 4 (concluded).

average and low concentrations with the 1200 GMT average. Kane exhibits the diurnal trend with smaller range and with less regularity, while McHenry shows a diurnal trend which is easily overridden by some other contributory factor.

Coshocton, on the open rolling terrain of east central Ohio, at an altitude of 354 m MSL, and Lewisburg, in the Greenbrier Valley (705 m MSL), are located where strong nocturnal inversions can be expected, although for different reasons. Such inversions effectively limit the vertical dispersion of ozone and permit its destruction by ground contact or surface-based emissions of destructive agents.

The McHenry monitoring location (altitude 884 m MSL) is higher than the surrounding terrain. The depth and intensity of the nocturnal inversion may be substantially less than would be observed at the other locations. Airflow over the rougher terrain could have more opportunity to weaken the inversions which occur, permitting the air at the ground at McHenry to become mixed with air from aloft, and to maintain higher ozone concentrations during the night.

Kane, although at the highest point within its locale (630 m MSL), is at a lower altitude than McHenry and is in smoother terrain. Nocturnal inversions may be deeper and the airflow smoother, so that ozone from aloft is not brought down as frequently as may occur at McHenry, and thus, increasing the diurnal range.

The time and type of frontal passage at each of the stations are indicated for July through September. At Kane, the ozone increases prior to cold frontal passages on July 10, 14 and 21, and decreases with or just after the front. Those fronts show sharp temperature contrasts to above 3 km.

At Coshocton, the limited evidence shows a similar relationship of ozone changes with fronts in July. The Lewisburg and McHenry records are incomplete in July. The strong association of ozone and fronts found at Kane is suspected to have occurred at McHenry, because of the intensity and depth of the fronts passing Pittsburgh.

In August and September, at all of the locations the ozone increases and decreases are weakly associated with frontal passages. The fronts are also weak and do not extend above 2 km.

The major stagnant high pressure situation occurred in conjunction with a high ozone episode in late August and early September. During this time, high ozone concentrations (> 200 $\mu g/m^3$) were observed at all the stations. At

Coshocton, a maximum value of 348 $\mu g/m^3$ at 0000 GMT on August 28, culminated a 36-hour period of ozone concentrations exceeding 275 $\mu g/m^3$. For eleven days, the twelve-hour average ozone concentrations exceeded 160 $\mu g/m^3$ at McHenry (see also Table 1).

Apparently, the subsidence aloft, associated with the stagnating anticyclone, contributes to the potential for high ozone concentrations, near the ground. Duration and intradiurnal changes are more of a local phenomena.

The descending motion and increasing ozone concentrations near the ground might be associated with a stratospheric ozone source. However, the evidence seems to the contrary. The slope of the 310°K θ surface at Pittsburgh indicates a descent rate of 2.2 km in 84 hours or 0.73 cm s^{-1}, which is too small for effective downward advection of ozone. Furthermore, the descending air tends to form a stable layer or an inversion inhibiting the vertical exchange of ozone.

After August 29, the inversion aloft dissipates, leaving the atmosphere below 5 km relatively unstable. Deep vertical mixing is quite possible. The stability is less at Pittsburgh than elsewhere, which may help explain the persistent ozone episode. The slow decrease of the ozone concentration is accompanied by the slow increase in the stability (as judged by the vertical separation of the 305 and 315°K surface).

In some instances, the ozone concentration increases when the θ near 3 km are decreasing in altitude (Kane-Buffalo in July). In some instances, these two variables increase or decrease together (McHenry-Pittsburgh in early August) or are lagged slightly (Coshocton-Dayton in August).

The Lewisburg-Huntington data pair maintains a character quite different from that of the other stations. The ozone concentration is strongly diurnal, but shows only occasional periods in excess of the standard, all occurring with the 0000 GMT averaging time. The occurrences of high and low ozone concentrations appear unrelated to the fronts, pressure systems, the vertical structure of the atmosphere, or to findings at other station pairs. One cause may well be the separation of the stations from one another. The cross-section data suggests that Huntington was in air more characteristic of the western slopes of the Appalachian Mountains whereas the trajectory data (Section 6) indicate Lewisburg was in air more characteristic of the eastern side. In retrospect, Greensboro, North Carolina might have been more representative of the airflow characteristic into Lewisburg.

5.0 OZONE CONCENTRATIONS AND THE MIXED LAYER

Transport and dispersion of atmospheric pollutants depend upon the properties of the mixed layer of the atmosphere. Friction and convective processes disperse the pollutant. The wind, changing with altitude, transports the material. Without prior knowledge of other similar efforts, the influence of the layer, as shown by its properties, on the ground level ozone concentration was examined. These properties were deduced from the rawinsonde ascents. The same pairings of ozone monitoring locations and rawinsonde locations are used.

This part of the study explores, from a statistical viewpoint, the influence of the boundary layer properties upon the average ozone concentrations, and their relative importance. If a parameter shows strong or consistent statistical influence or correlation with ozone, a physical reason may be indicated which, in turn, may help "explain" high ozone concentrations in nonurban locations.

There are necessarily some dangers in extrapolating mixed layer properties from Buffalo to Kane, or any of the other three data pairs. Mixing depth in central Pennsylvania is not the same as near the shore of Lake Erie. Lacking anymore detailed information, it is necessary to assume that the properties of the mixed layer at the rawinsonde station and the nonurban locations are the same.

5.1 Mixing Layer Parameters

The research sought to relate the observed ozone concentrations to the properties of the atmospheric boundary layer; i.e., the mixing depth of the air, mean water vapor mixing ratio, vector mean wind speed through the mixing layer, and the parameter χ/Q, and the ventilation index for each of the soundings. The mixing depth, Z_{mix}, as defined by Holzworth[11], is the thickness of the air between the ground and the intersection of the adiabatic temperature with the sounding temperature. In the morning (1200 GMT), the adiabatic temperature is given by the potential temperature of the overnight minimum temperature plus 5°C. In the afternoon, it is given by the potential temperature corresponding to the maximum afternoon temperature. The mixing depth indicates the depth to which mixing due to daytime heating will occur. When the mixing depth is large, the pollutants should have ample opportunity to disperse upward. Usually, these conditions are also associated with superadiabatic or slightly unstable layers of the afternoon. A small mixing depth indicates poor vertical dispersion of pollutants, thereby tending to increase their concentration near the ground.

The mean water vapor mixing ratio of the air through the mixed layer, R_{mix}, gives the indication of the amount of water vapor in the air. During well-mixed conditions, the mixing ratio should be nearly uniform, since it is a conserved quantity.

Through the depth of the mixed layer, the wind speed, S, and direction, α, may change with altitude. To approximately the mean transport by the wind, the vector average wind speed and direction for the mixed layer was computed from the average west (u), and south (v) wind components for the layer. Although the trajectory plots showed direction and speed of air movement prior to arrival, u and v or S and α show the dependence of the ozone concentration upon the existing wind velocity.

Average value, $\bar{q}$, of a scalar quantity, q, for the mixed layer was computed by the formula

$$\bar{q} = \sum_{i=2}^{J} \left[(q_i + q_{i-1}) \cdot (z_i - z_{i-1})\right] \Big/ 2 \cdot Z_{mix}$$

where J was the number of data points required to define the mixing layer.

The ventilation index, V, is defined by the mean wind speed through the mixed layer times the depth of the mixed layer. It measures the flux of air into an area.

Partly to compare the summer of 1973 data with other climatic data, and partly to include a regression analyses, the quantity χ/Q, as defined by Holzworth for a city of cross-section 100 km was computed for each sounding. χ/Q represents the relative dispersion of pollutants downwind of a major city and is a function of the mixing depth and the mean wind speed.

5.2 Regression Analyses

The research tried to ascertain the properties of the mixed layer having the greatest influence on the twelve-hour average ozone concentration. Initially, one might assume that, since high ozone concentrations occurred during the late afternoon and early evening when mixing depth and wind speed are greatest, and that since low ozone concentrations occurred during the morning when the mixing depth and wind speeds are small, that the mixing depth or the ventilation index, or both, might be good predictors of the ozone concentration as was found in New York.[12] However, that assumption should be tested against the data. Other variables or combination of variables may prove better indicators.

Selection of the boundary layer parameters which most strongly are associated with the high or low ozone concentration was accomplished using a regression analysis of the ozone concentration as a linear function of mixed layer parameters. In Model I, the parameters are Z_{mix}, R_{mix}, S, α, χ/Q, V and in some cases the hour (0000 or 1200 GMT). In Model II, the mean wind components, u and v, were used instead of α and S. All the other variables remained the same. The regression procedure chosen was the "Maximum R^2 Improvement". R is the linear correlation coefficent of the regression. The procedure is described in the "User's Guide to the Statistical Analysis System"[13] in the following manner:

> "Maximum R^2 Improvement. This technique was developed by James H. Goodnight; he considers it superior to the stepwise technique and almost as good as calculating regressions on all possible subsets of the independent variables. Unlike the three techniques above, this technique does not settle on a single model. Instead, it looks for the 'best' one-variable model, the 'best' two-variable models, and so forth. It finds first the one-variable model producing the highest R^2 statistic. Then another variable, the one which would yield the greatest increase in R^2, is added. Once this two-variable model is obtained, each of the variables in the model is compared to each variable not in the model. For each comparison, the procedure determines if removing the variable in the model and replacing it with the presently excluded variable would increase R^2. After all the possible comparisons have been made, the switch which produces the largest increase in R^2 is made. Comparisons are made again, and the process continues until the procedure finds that no switch could increase R^2. The two-variable model thus settled on is considered the 'best' two-variable model

the technique can find. The technique then adds a third variable to the model, according to the criteria used in adding the second variable. The comparing and switching process is repeated, the 'best' three-variable model is discovered, and so forth."

The procedure also chooses the "best" N-variable model for which the terms are significant at the 0.1000 level. Figure 5 shows typical output of the procedure.

5.3 Results

Table 3 is a summary of the number of terms of the "best" model, its correlation coefficient to the ozone concentration, and the relative importance or the ranking of the variables making up that "best" model. The model for Lewisburg ozone concentrations uses the Huntington mixed layer data, etc. For Kane and McHenry ozone stations, the data were further stratified by the observational period so that only 0000 GMT data are used in the analysis or only 1200 GMT data are used on the analysis. The regressions included only those date/times when all of the model variables were available for a measuring location.

The mean water vapor mixing ratio of the mixed layer, R_{mix}, is the most significant variable of either model for three of the data sets. Stated alternatively, of the variables tested, R_{mix} is the best single predictor of the twelve-hour ozone concentrations. This was a most surprising result. Furthermore, the correlation coefficient of R_{mix} and ozone is positive (Table 4), meaning that ozone increases when R_{mix} increases. If the high ozone concentrations near the ground were a result of vertical transport or diffusion from the stratosphere, then the same processes would have brought water vapor down also. The stratosphere is quite dry ($\sim 2g\ kg^{-1}$ maximum) and water vapor mixing ratio is conserved in descending motion. Stratospheric ozone would, therefore, be associated with a small mixing ratio--contrary to the observations. Thus, the stratosphere does not appear as a feasible principal source of ozone during the episodes of high mixing ratio (and high ozone concentration)."

The mixing depth also appears as a variable which should be considered. There is inconsistency in its importance between the data pairs (e.g., ranking 1 and 2 for McHenry and unranked at Kane).

```
                         MC HENRY OZONE AND PITTSBURG RAOB DATA  0000 GMT

                       STEPWISE REGRESSION PROCEDURE FOR DEPENDENT VARIABLE OZONE

NUMBER IN     R-SQUARE      VARIABLES IN MODEL
  MODEL

   1        0.17399817      ZMIX

   2        0.38187667      ZMIX RBAR

   3        0.42671815      ZMIX RBAR VENT

   4        0.45650071      ZMIX RBAR DIR VENT

THE VARIABLES IN THE ABOVE MODEL HAVE ALL BEEN DEEMED SIGNIFICANT AT THE  0.1000 SIGNIFICANCE LEVEL

ANALYSIS OF VARIANCE TABLE , REGRESSION COEFFICIENTS , AND STATISTICS OF FIT FOR THE ABOVE MODEL


SOURCE               DF      SUM OF SQUARES       MEAN SQUARE        F VALUE    PROB > F      R-SQUARE          C.V.

REGRESSION            4      78150.80426561    19537.70106640       13.01890      0.0001    0.45650071     24.57693 %

ERROR                62      93044.55752543     1500.71866977

CORRECTED TOTAL      66     171195.36179105



SOURCE             . DF       SEQUENTIAL SS         F VALUE     PROB > F          PARTIAL SS        F VALUE     PROB > F

ZMIX                  1      29787.67979192        19.84894       0.0001    48719.47032572       32.46409       0.0001
RBAR                  1      35586.80782241        23.71318       0.0001    36025.66673208       24.00561       0.0001
VENT                  1       7677.67970762         5.11600       0.0256     8769.29246057        5.84340       0.0176
DIR                   1       5098.63694367         3.39746       0.0667     5098.63694367        3.39746       0.0667



SOURCE        .          B VALUES           T FOR H0:B=0            PROB > |T|            STD ERR B        STD B VALUES

MEAN                 -23.78907023
ZMIX                   0.05503156                 5.69773               0.0001           0.00965851          0.59034630
RBAR                   9.05694901                 4.89955               0.0001           1.84852595          0.48206365
VENT                  -0.00168726                -2.41731               0.0176           0.00069799         -0.24458599
DIR                    0.10491502                 1.84322               0.0667           0.05691939          0.17973692
```

Figure 5. Sample results of maximum R^2 improvement technique choosing the best regression model.

Table 3. RANKING, BY SIGNIFICANCE, OF MIXED LAYER VARIABLES, IN AN N-TERM LINEAR REGRESSION MODEL OF OZONE CONCENTRATIONS

MODEL I

	"Best" Model		Variables/Ranking						
O_3 Site	Terms	Corr. Coeff.	Hr	Z_{mix}	R_{mix}	Wind Speed	Dir	χ/Q	V
Lewisburg	4	0.597	2	1	3	4			
Coshocton	4	0.573	1	4	2			3	
Kane	4	0.619	1*		1*	4		3	
McHenry	4	0.676	NI	1*	1*	3	4		
Kane (00)	1	0.509	NI		1				
Kane (12)	2	0.610	NI		1			2	
McHenry(00)	4	0.676	NI	1*	1*		4		3
McHenry(12)	2	0.742	NI	2	1				

*Significant at 0.0001

NI - Not Included in the Model.

Table 3 (continued).

MODEL II

	"Best" Model		Variables/Ranking						
O_3 Site	Terms	Corr. Coeff.	Hr	Z_{mix}	R_{mix}	u	v	χ/Q	V
Lewisburg	4	.613	2	1	4	3			
Coshocton	6	.592	1	4	2		5	3	6
Kane	4	.624	1*		1*	3		4	
McHenry	4	.667	NI	1*	1*	4			3
Kane (00)	3	.572	NI	3	1		2		
Kane (12)	2	.610	NI		1			2	
McHenry (00)	4	.678	NI	1	1	4			3
McHenry (12)	3	.770	NI	2	1		3		

Table 4. LINEAR CORRELATION COEFFICIENT, R, OF EACH MIXED LAYER VARIABLE WITH TWELVE-HOUR OZONE CONCENTRATION

	Variables								
O_3 Site	HR	Z_{mix}	R_{mix}	u	v	χ/Q	V	S	α
Lewisburg	-0.53	0.53	0.01	-0.10	-0.05	-0.20	0.30	0.02	0.04
Coshocton	-0.41	0.41	0.25	0.11	0.20	-0.10	0.23	+0.00	0.12
Kane	-0.32	0.08	0.47	0.19	0.13	-0.12	0.03	0.11	0.08
McHenry	NC*	0.38	0.39	0.10	-0.02	-0.05	0.08	-0.18	0.25
Kane (00)	NC	-0.13	0.51	0.25	0.38	-0.02	-0.07	0.11	-0.04
Kane (12)	NC	-0.13	0.59	0.09	-0.00	-0.01	-0.10	-0.06	0.16
McHenry (00)	NC	0.42	0.33	-0.04	-0.09	-0.08	-0.08	-0.23	0.16
McHenry (12)	NC	-0.24	0.69	0.27	0.14	0.13	-0.21	-0.18	0.25

*NC - Not Computed

The lack of a decided directional (α or u or v) preference (Table 4) at any of the locations implies that the direction of the air flow during the averaging period had little relationship to the amount of ozone measured. Thus, the recent (six to twelve hour) location of an air parcel does not seem to determine the ozone content. Wind speed, S, shows only a weak and inconsistent relationship to the ozone concentration. The mixing depth also ranked high in relationship to the ozone concentrations. Wind speed, direction, relative dispersion of the atmosphere, and the ventilation at the rawinsonde locations are poorly correlated to the amount of ozone measured at the associated monitoring location.

The rate of synthesis or destruction of ozone in the presence of water vapor alone may be written

$$\frac{1}{O_3} \frac{dO_3}{dt} = k(O_3, R_{mix}) \cdot R_{mix} \qquad (5.1)$$

where O_3 is the ozone concentration

R_{mix} is the water vapor concentration, and

$k(O_3, R_{mix})$ is the rate coefficient for the reaction.

A regression analysis of the local percentage change of ozone with time as a function of R_{mix} should give a straight line of slope k if the synthesis or destruction of ozone depends solely upon the amount of water vapor present.

To test the hypothesis that the rate of change of ozone is independent to the water vapor content, a maximum R^2 analysis was run except that the percentage change of ozone at McHenry from one twelve-hour period to the next was used instead of the ozone concentration. That analysis picked Z_{mix} and the wind direction, α, as the only two variables of the "best" model. The correlation coefficient of the model was only 0.49. The correlation coefficient of the percentage change of ozone with water vapor mixing ratio was - 0.02, indicating that the two factors are not linearly related. It must be remembered, however, that the twelve-hour ozone data and the mean water vapor mixing ratio of the mixed layer were used in the analysis. At a much smaller time period, such as five minutes, the production of ozone may be related to the amount of water vapor present.

At this time, it is not known whether the correlation of ozone concentration to R_{mix} is only statistical or whether there is a physical basis for it.

Dr. Lyman Ripperton of RTI suggests that the presence of water vapor influences the production of hydroxyl (OH) radicals in the ozone production process[14]. These reaction rates are such that the water vapor may be a contributing factor to the high ozone. A definitive answer awaits further experimentation and evidence.

6.0 OZONE CONCENTRATIONS AND AIR PARCEL TRAJECTORIES

Previous research[9] suggested that the high ozone concentrations might be associated with air which had passed near one or more urban-industrial areas, where ozone and/or its precursor might be abundant. The average annual hydrocarbon emission density shown in Figure 6 is used as a guide to the source of anthropogenic ozone precursors. Major urban-industrial areas are associated with the larger emission densities. Trajectories, showing the path of an air parcel for 48 hours prior to its arrival at one of the four ozone monitoring locations, were computed for each 0000 GMT and 1200 GMT between July 3 and October 31. The plotted trajectories are presented in Appendix B.

6.1 Computation of Trajectories

A computer program to compute the air parcel trajectories was made available to RTI by Mr. John Clarke, Division of Meteorology, EPA. This program was modified to meet the specific needs of this research. The program interpolates in time (linearly) and in space ($1/R^2$ weighted, using the three nearest observations) for the value of the u and v wind components at a given location. The corresponding 2-hour latitude and longitude displacements of the parcel are computed, and the "new" position, two hours previous to the "old" position is found. Wind components are interpolated for the new position and time.

Winds for the trajectory analysis were taken from the 22 rawinsonde stations at 900 mb, approximately 1 km above mean sea level, for each 12-hourly observation during the four-month period. The 900-mb level is usually within the mixed layer during the afternoon and very near the top of surface-based inversions during the nighttime hours. It was not known *a priori* whether the inversions would be above or below this altitude.

The trajectories computed in this manner are only approximations to the actual path taken by the air parcels because of errors in the assumptions, techniques, and measurements. Daytime mixing and terrain characteristics cause the air to rise and fall relative to the ground, so that one air parcel does not stay at 900 mb throughout the travel time. The variable terrain of the study area also means that the 900 mb level is not a fixed distance above the ground. The analysis technique tends

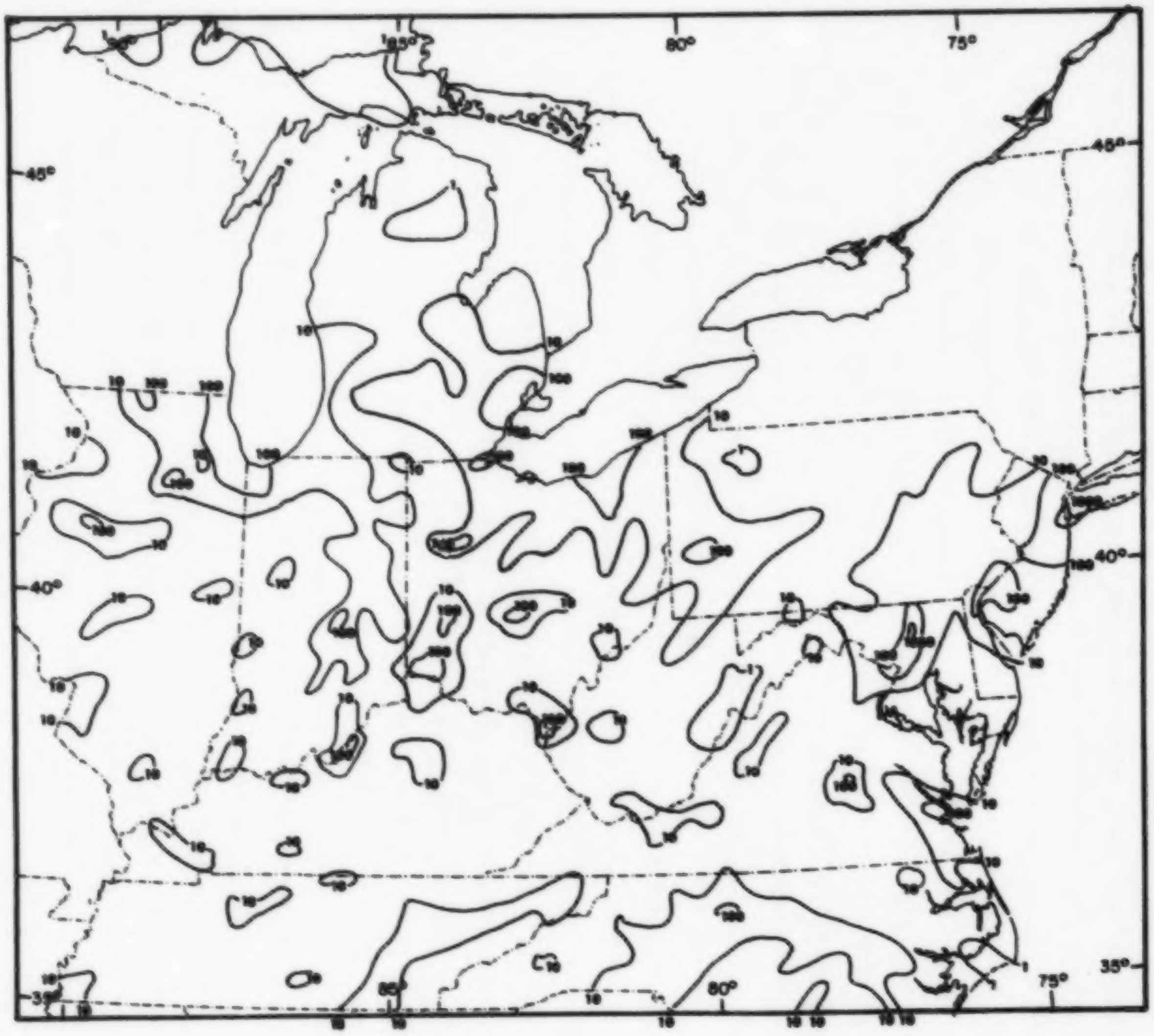

45°
40°
35°
90°
85°
80°
75°
10
100
1000

Figure 6. Average annual hydrocarbon emission density, 1970, tons mi^{-2}.

to smooth data by interpolation and loses contrast across fronts or shear lines, which have important impact upon the initial wind directions and hence, all of the resulting trajectories. Errors of the reported winds may be ± 1 m s^{-1} and ± 2 degrees in direction. In light and variable winds, the errors may be much larger. The plotted trajectories should be thought of as the "best estimate" of the actual path taken, but with increasing uncertainty as the time and/or distance from the origin increases.

6.2 Selection of Trajectories

Since "high" or "low" ozone concentrations may have a different meaning for each monitoring location, the highest (upper decile) and lowest (lowest decile) ozone concentrations were determined for each monitoring location, (see Table 5). Trajectories associated with ozone concentrations in these deciles were plotted on a common map for each location and are presented in Figure 7.

6.3 Trajectories with High and Low Ozone Concentrations

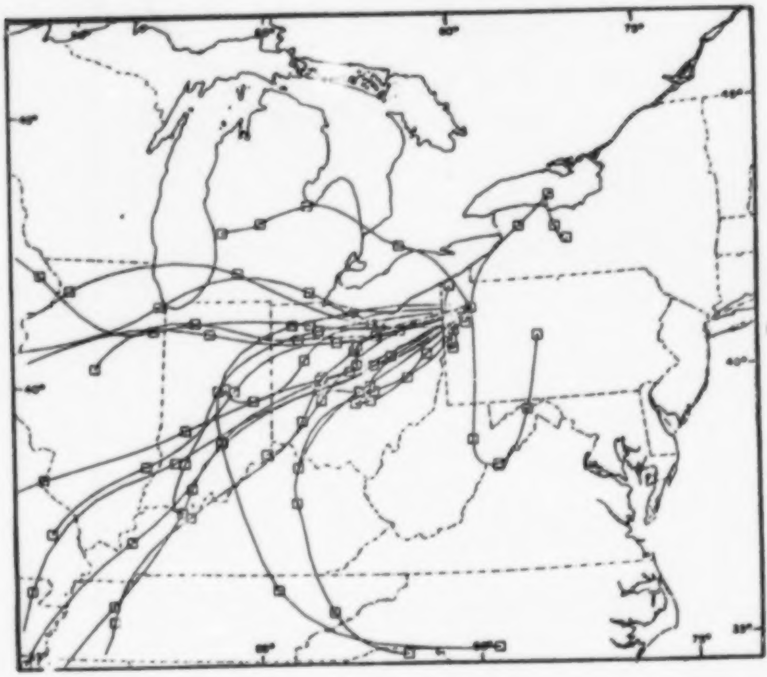
6.3.1 Kane

High ozone concentrations at Kane are associated with trajectories from the west and west southwest, passing over central Ohio and funneled down toward Kane. Only three of the trajectories come from other directions. The positions twenty-four hours prior to arrival, extend westward to nearly the Indiana-Illinois border, northward to the very southern part of lower Michigan and remain almost exclusively north of the Ohio River Valley. Thus, in almost every instance, a high ozone concentration at Kane is associated with the trajectory over central or northern Ohio during the immediately previous twenty-four hours.

The trajectories associated with low concentrations at Kane are predominantly from the northwest, principally across the southern portion of Michigan and from Wisconsin. Several cross central Ohio. Thus, with several exceptions, it seems that the air trajectory may strongly influence the ozone concentration at Kane. Parcel speeds prior to arrival in the low ozone cases are quite variable, some moving fast, others slowly. In general, the low ozone concentrations are associated with higher wind speeds than are the high ozone concentrations.

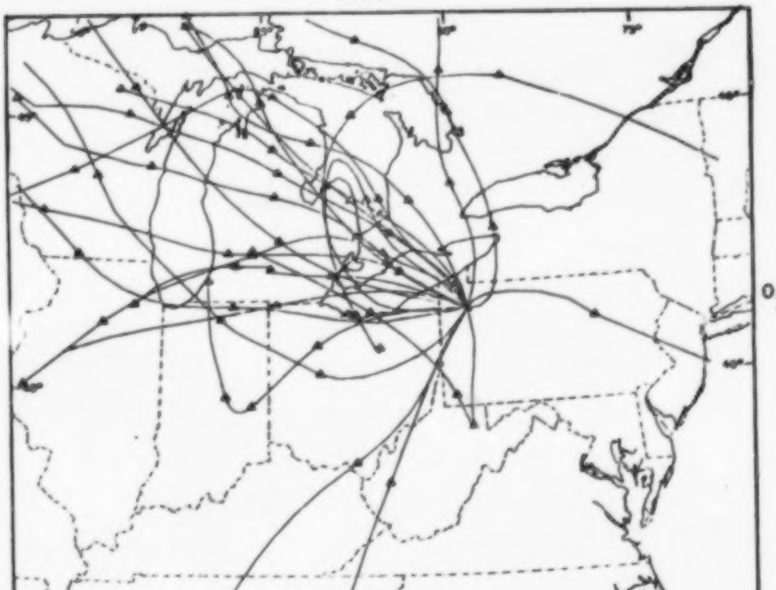
Table 5. OZONE CONCENTRATIONS (μgm^{-3}) FOR INDICATED PERCENTILE RANKINGS AT EACH MONITORING LOCATION.

	Percentile				
STATIONS	10	30	50	70	90
McHenry	86	112	140	168	218
Kane	64	92	121	150	190
Lewisburg	58	76	93	112	150
Coshocton	47	70	93	123	165
All Stations	60	85	110	139	182



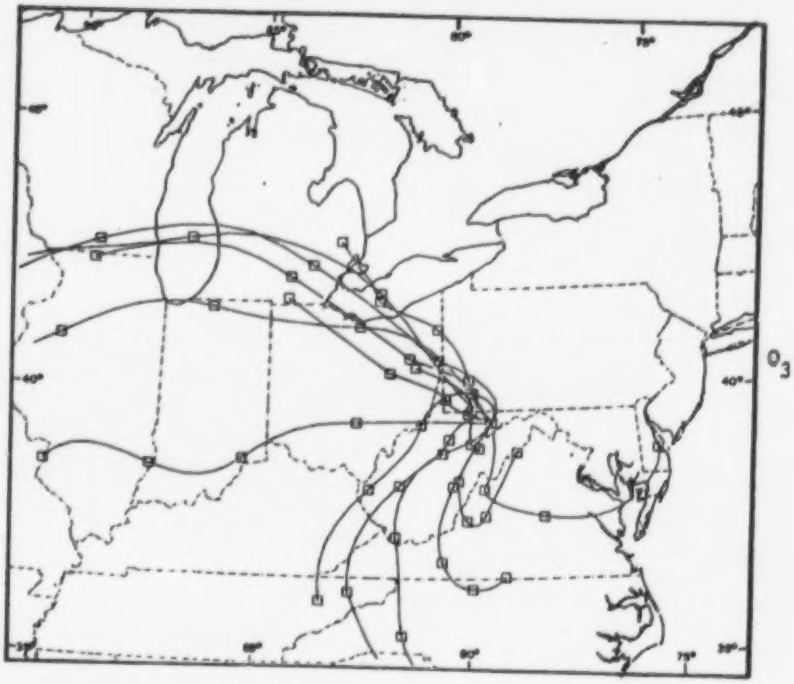
80°
75°
90°
40°
35°
O_3 > 190 μgm^{-3}

Kane



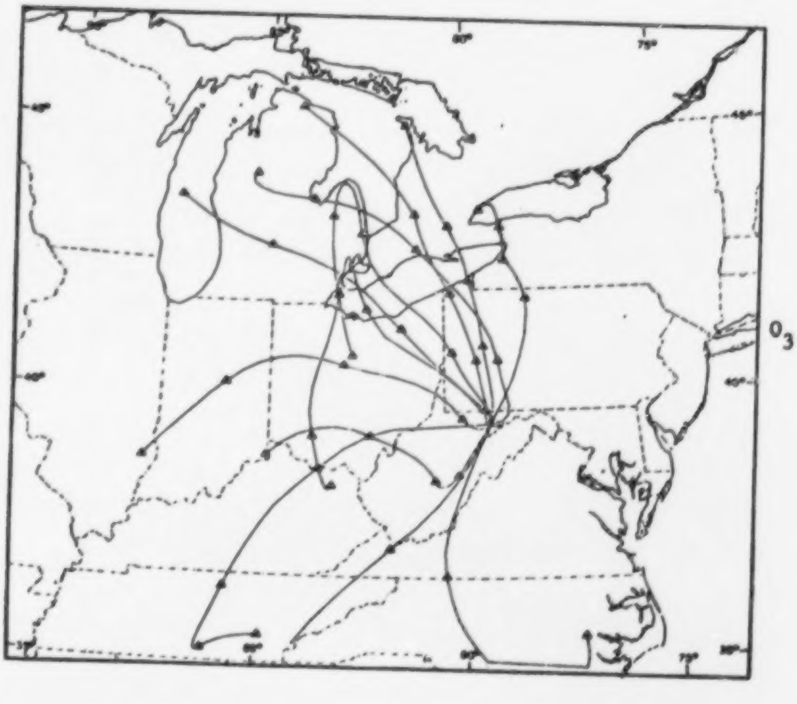
80°
75°
90°
40°
35°
O_3 < 64 μgm^{-3}

Figure 7. Trajectories associated with high and low at the indicated location. Squares (□) and triangles (Δ) indicate the twelve-hour positions prior to arrival.


90°
85°
80°
75°
45°
40°
35°

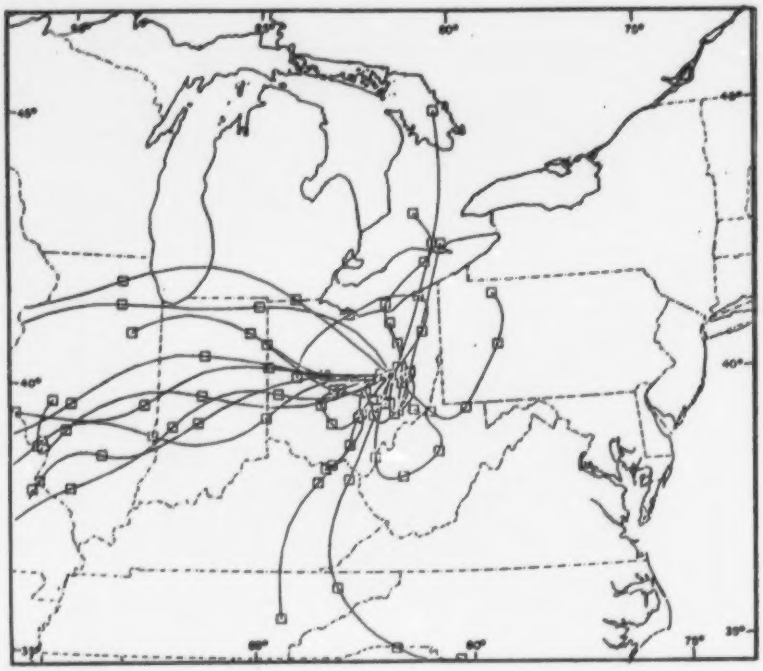
$O_3 > 218\ \mu gm^{-3}$

McHenry


90°
85°
80°
75°
45°
40°
35°

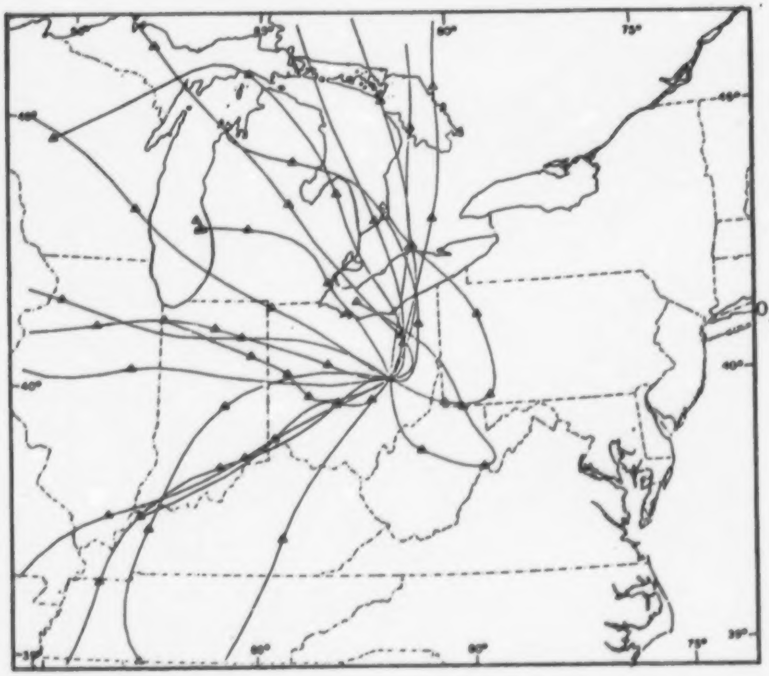
$O_3 < 86\ \mu gm^{-3}$

Figure 7 (continued).



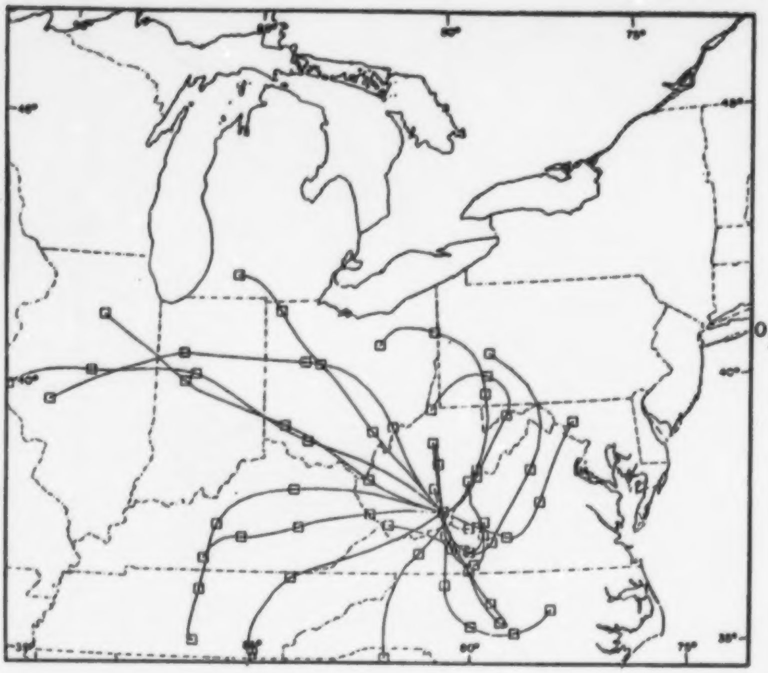
$O_3 > 165\ \mu gm^{-3}$

Coshocton



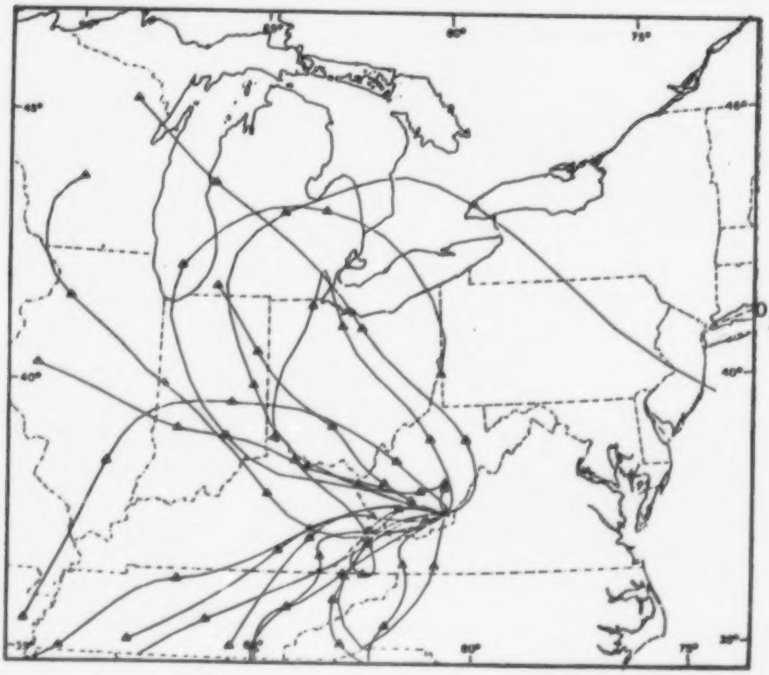
$O_3 < 47\ \mu gm^{-3}$

Figure 7 (continued).


80°
75°
45°
40°
35°

$O_3 > 150\ \mu gm^{-3}$

Lewisburg


80°
75°
45°
40°
35°

$O_3 < 47\ \mu gm^{-3}$

Figure 7 (concluded).

6.3.2 McHenry

High ozone concentrations arriving at McHenry appear to come from two general areas. One area is typical of northwest flow over industrial southern Michigan and northeastern Ohio where hydrocarbon emissions are large. The air seems to move fairly rapidly over this area before arriving at McHenry. The second area is to the southwest, with the air moving across West Virginia into McHenry at slow speeds on the trailing side of a high pressure system. Over the past 48 hours, these trajectories have been over the smallest hydrocarbon emission density area of the northeastern quarter of the country. With three exceptions, trajectories associated with low ozone concentrations at McHenry are indicative of slow moving air, principally flowing from the northwest into McHenry across northeastern Ohio and southwestern and western Pennsylvania. That situation is a stark contrast to the faster-moving trajectories which arrived at Kane from the northwest. The three exceptions are air parcels which arrived from the southwest rapidly passing over West Virginia, where slow-moving air had shown higher ozone concentrations. The slower moving trajectories moved at an average speed of 6 m s^{-1} or less for the 48 hours prior to arrival. Many of these trajectories passed near the Pittsburgh, Pennsylvania area.

6.3.3 Coshocton

High ozone concentrations arrived at Coshocton from all directions but principally from the west. These westerly trajectories indicate speeds of 12 to 15 m s^{-1}, traversing the distance from central Illinois to Coshocton in a period of about 24 hours and are associated with the ozone episode during late August. Clustered about Coshocton are many trajectories that loop back upon themselves, indicating that stagnant air conditions are associated with the other high ozone concentrations.

Most of the low ozone concentrations at Coshocton are associated with rapidly moving air parcels arriving from the north to northwest and from the southwest. Some air parcels cross the same areas associated with high ozone concentrations. Thus, these data suggest that the speed of parcels is correlated to the extreme ozone concentrations observed at Coshocton; i.e., high wind speed--low ozone concentration, low wind speed--high ozone concentration.

6.3.4 Lewisburg

High ozone concentrations at Lewisburg are associated with trajectories coming from all directions and with apparently equal frequency. Each trajectory shows a very definite anticyclonic curvature indicating that the high concentration was associated with a slow-moving anticyclone probably passing to the north of the Lewisburg area.

The low ozone concentrations at Lewisburg are associated with trajectories which arrived from the southwest through west and northwest. Most of the trajectories indicated fairly rapid air movement across industrialized areas, but moving more slowly approaching Lewisburg. This pattern, as was the case with the high ozone concentrations, is unlike patterns observed at the other three stations. Thus, Lewisburg appears in a different circulation pattern associated with the high and low ozone concentrations. The result is not surprising since two of the stations are located to the west of the Appalachian Mountains and the third is along the ridge line of the Appalachians and Lewisburg is on the eastward side of the ridge in anticyclonic circulation.

6.4 Summary

The trajectory analyses do not implicate one particular area of the northeastern United States as a source of high ozone or ozone precursors concentrations at the four sampling locations. There are common regions for some stations, such as northeastern Ohio; but air coming from the Lake Erie-Lower Michigan regions appears favorable for low ozone at Kane, but high ozone at McHenry.

Slow-moving air parcels tend to be associated with higher ozone concentrations and vice versa. However, the characteristics of the mixed layer wind speed and direction were not dominant variables in the regression analysis. The trajectories associated with high or low ozone do not indicate a preference having a maritime origin or any other indication that they might be associated with a high or low water vapor content.

7.0 CLIMATIC INFLUENCES

The influence of changes of climatic variables upon ozone concentrations is not clearly understood. Nevertheless, investigations of two variables measured at Elkins, West Virginia, for comparison with McHenry data show the following:

7.1 Temperature

Temperatures in July and August 1973 were 1 to 2°F warmer during 1973 than in 1972. The 1973 temperatures very nearly equal to the 30-year mean. September 1972 was 2°F warmer than in 1973. Although the results of Section 8.1, show the higher daily maximum temperatures are associated with higher ozone concentration the small temperature differences seem insufficient to explain the differences in ozone concentrations from 1972 to 1973.

7.2 Average Sky Cover, Sunrise to Sunset

The average sky cover, from sunrise to sunset is the only indication of solar radiation amounts reported in the Elkins LCD. In July, August and October of 1972, monthly average sky cover exceeded the 1973 monthly average by at least one-tenth sky cover, whereas the September data differed by only 0.1 tenth. The 1973 data exceeded the long-term mean values in July and August, 1973 and are within 0.1 tenth of the mean the other two months.

These indications suggest that more solar radiation was available in 1972, perhaps meaning a greater potential for ozone generation. However, the reported sky cover does not discriminate between high, possibly thin, cirrus clouds or low-level stratus. An increase in the former probably does not substantially reduce the incoming radiation needed for ozone generation, whereas the latter may reduce the ultraviolet light.

7.3 Relative Dispersion

Holzworth's climatology of the dispersion characteristics of the mixed layer (χ/Q) were compared with computations of χ/Q at the four rawinsonde stations. The computed values for the Dayton and Pittsburgh soundings are compared with Holzworth's summer and autumn seasonal statistics in Table 6. At Dayton, the afternoon soundings indicate good dispersion with small variations from the climatological values.

Table 6. MEDIAN, UPPER QUARTILE AND UPPER DECILE VALUES OF χ/Q ($s\ m^{-1}$) VALUES OBSERVED IN 1973 AND CLIMATOLOGICAL VALUES

Season	Dayton			Pittsburgh		
Time	Median	Upper Quartile	Upper Decile	Median	Upper Quartile	Upper Decile
Summer*	62	174	420	96	458	740
Morning	*65*	*165*	*260*	*44*	*122*	*206*
Autumn*	70	173	394	61	380	820
Morning	*96*	*215*	*410*	*80*	*230*	*488*
Summer	16	19	25	15	18	21
Afternoon	*17*	*22*	*30*	*16*	*22*	*30*
Autumn	16	21	28	16	21	26
Afternoon	*17*	*23*	*30*	*18*	*25*	*35*

*Summer - June, July, August - Climatological Data (after Holzworth)
July, August - 1973 Data (italics)

*Autumn - September, October, November - Climatological Data
September, October - 1973 Data (italics)

The summer morning values of 1973 showed somewhat better dispersion (lower values of χ/Q), while the climatological dispersion is slightly better during the autumn.

Dispersion at Pittsburgh was substantially better than climatology suggests during the summer mornings of 1973. The autumn morning values, unlike those at Dayton showed better dispersion than Holzworth reported. Although the afternoon χ/Q at Pittsburgh showed poorer-than-normal dispersion, the differences do not seem important compared to the differences of the morning values.

These results suggest slightly better overall dispersion during the study period during the morning than might be expected from climatology. Since χ/Q does not exert much influence on the nonurban ozone concentrations, according to the regression analysis, the better dispersion has little relevance to explaining the high ozone concentration in 1973.

The basis for assessing an impact of climatic differences has not been established because 1) there are insufficient ozone concentration measurement to establish a climatology for one, and 2) the impact of weather elements upon that climatology is not known. The reasons for differences in ozone concentrations at McHenry in 1972 and 1973 remain unresolved.

7.4 Stagnation Periods

Despite the generally favorable dispersion conditions, for the season, the prolonged stagnation period of late August into September surely contributed to the increased frequency of exceedance of the NAAQS for ozone over that frequency in the data taken in 1972. That event was unprecedented in any summer of the past nine years according to data published in the Climatological Data, National Summary. During the 1972 measurement period at McHenry, Maryland, high pressure systems did not stagnate but moved slowly through the study region at a nearly constant rate.

8.0 SELECTED STUDIES

8.1 Maximum Temperature and Maximum Ozone

Jeffries'[16] experimental results show that when the daily maximum temperature remains below about 60°F (15.4°C) the generation of ozone concentration above 160 $\mu g\ m^{-3}$ did not occur. The correlation of the maximum hourly ozone concentration for a given day (midnight to midnight) as a function of the maximum daily temperature was investigated for each of the four ozone monitoring stations. Since temperature was not an observed quantity at each location throughout the period, daily maximum temperature data were extracted from the Local Climatological Data Summary for Beckley, West Virginia, Elkins, West Virginia, Youngstown, Ohio, and Columbus, Ohio. These temperatures were correlated with the Lewisburg, McHenry, Kane and Coshocton ozone concentrations, respectively.

The scatter diagrams and linear regression line for each temperature ozone station pairs are given in Figure 8. In all cases, an increase of maximum hourly average ozone occurs with increasing temperature, but in none of the instances was an ozone concentration greater than 160 $\mu g\ m^{-3}$ found with temperatures less than 16.5°C. Of the four cases, the best correlation (0.710) of the data occurred with the McHenry-Elkins pair of data, whereas the poorest correlation of 0.526 occurred with the Lewisburg-Beckley data set. The greatest slope of the regression line also occurs with the McHenry-Elkins data (11.95 $\mu g\ m^{-3}\ K^{-1}$) and the smallest slope with the Lewisburg-Beckley data (5.02 $\mu g\ m^{-3}\ K^{-1}$). The correlation coefficient for the Kane-Youngstown data pair was 0.664 and for the Coshocton-Columbus data pair was 0.707.

In summary, these data confirm Jeffries' experimental findings in the free air. However, the trend for higher ozone concentrations with greater maximum temperatures does not establish that the ozone concentration is a function of the maximum temperature since the maximum temperature is a function of other meteorological variables, including the sky conditions, synoptic weather features, and the past history of the air.

8.2 Concurrent Trajectories

Trajectories that arrived at a particular station may pass very near or over one ozone monitoring station enroute. Such instances

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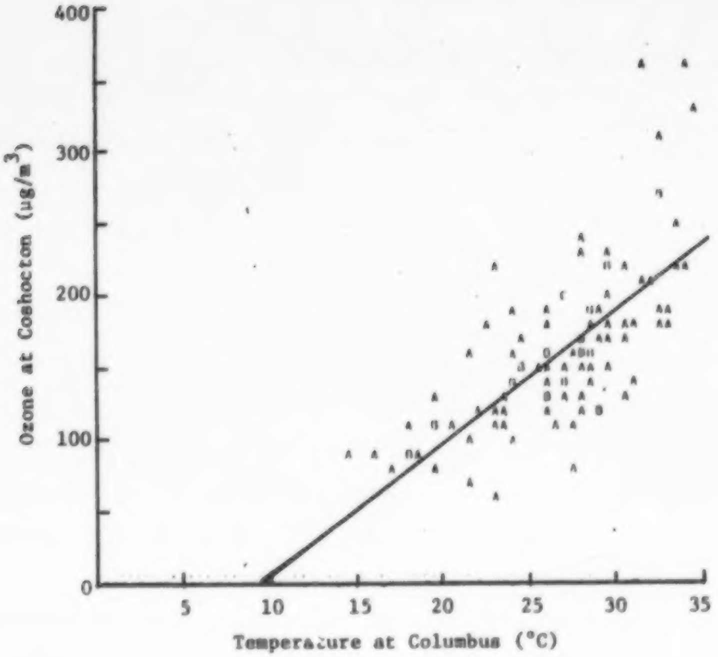


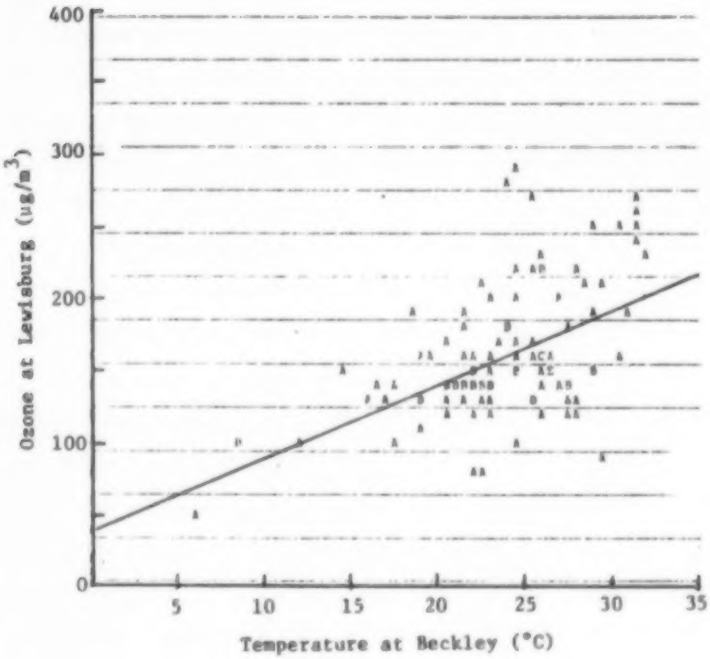
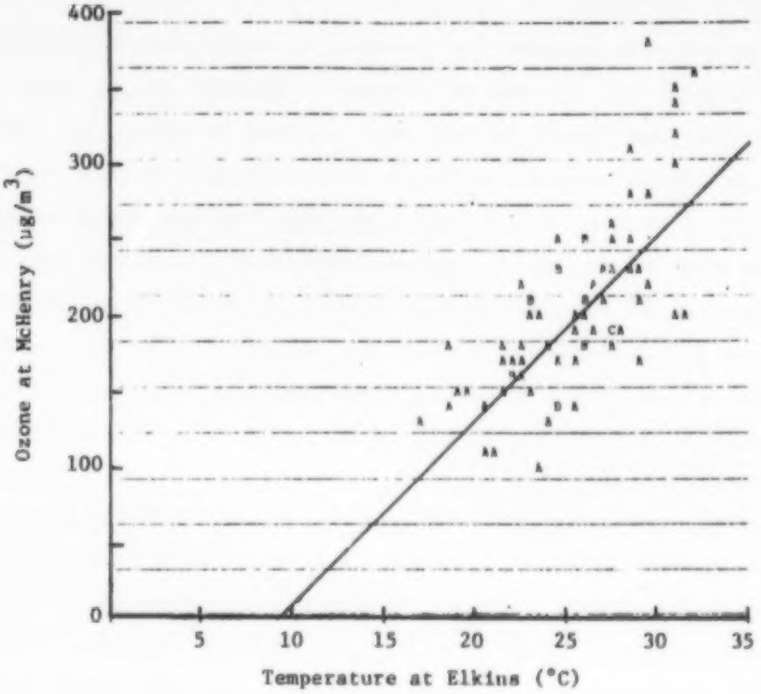


Figure 8. Scatter diagrams and least square linear fit of daily maximum hourly ozone and daily maximum temperature at indicated locations. (A-1 data point; B-2 data points, etc., fall within the 0.5°C temperature and 10 μg/m^3 ozone concentration increment).



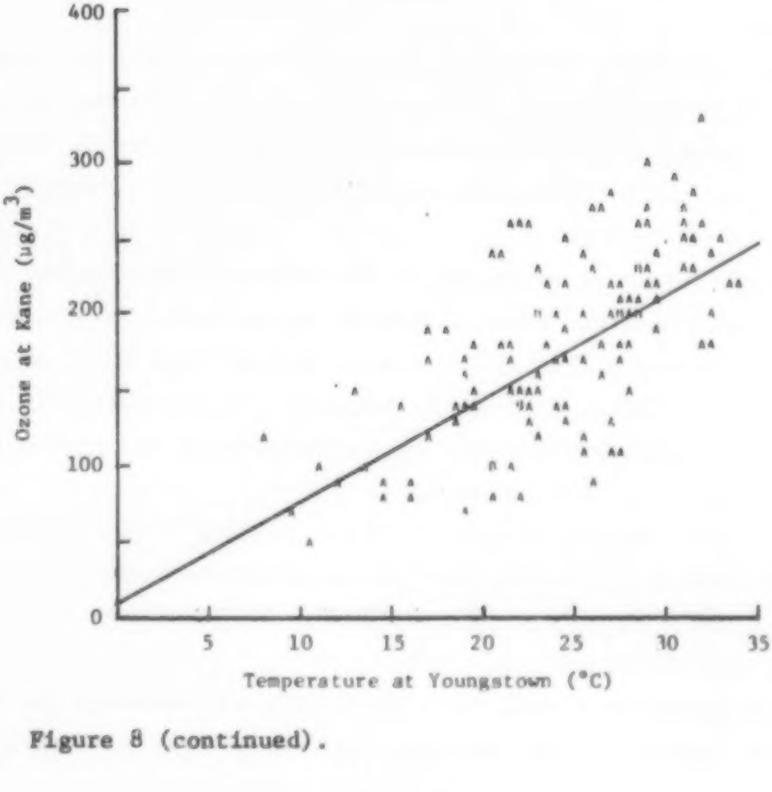


Figure 8 (continued).

afford an opportunity to examine the changes in ozone concentration as the parcel moves from one station to another. Because of the uncertainty in the precise time the parcel passed over a given location, if indeed it did, a period approximately two hours before to two hours after it passed one location is compared to the four-hour average concentrations centered on the time of arrival. Travel times were estimated from the plotted trajectory. No specific criteria were established to define "passing near an indicated ozone monitoring station." The percentage change in concentration with time as a parcel moved along a path is an indication of net synthesis or destruction of the ozone. The data obtained for this analysis are presented in Table 7.

A consistent, characteristic change from one station or another or among the various stations as a function of time or as a function of ozone concentration was not found. Changes of ozone concentration in a parcel enroute from one position to another, in given length of time, are situation dependent. More factors must be considered than just the ozone change, especially the relevance of the computed change of ozone.

8.3 Case Study

The prolonged stagnation period with persistent high ozone concentration, August 25 to September 5, was the most significant event of the field measurement program. Although a thrust of the research was to investigate for consistent meteorological ozone relationships in all situations, this event deserves some comment.

According to the data of Figure 3, the surface high pressure center moved across Kentucky: then between McHenry and Coshocton on the morning of August 29th: became stationary near Kane on the 30th: and reached its maximum sea level pressure 1031 mb on the 31st. By the next day, the center drifted almost over McHenry, and remained there for five more days, slowly decreasing in central pressure.

Figure 4 shows warming at each of the four rawinsonde stations. The warming period begins about the 25th and persists until the cold front of September 5, 6 and 7 traverses the area (Table 2). The warm core high is further indicator of stagnant conditions.

The trajectories show that there was little air movement in the 48 hours prior to August 25. For the next three days, the air flow becomes

Table 7a. CHARACTERISTICS OF AIR PARCELS ARRIVING AT KANE AFTER PASSING NEAR THE INDICATED OZONE MONITORING LOCATIONS.

From Coshocton

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
7-27-12	6	.0574
8-2-00	18	.0380
8-7-12	12	-.0443
8-8-00	12	.1730
8-31-12	6	-.1007
9-1-00	10	.0614
9-1-12	14	-.0382
9-27-12	12	-.0419

From Kane

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-14-12	18	- .0179
8-19-12	44	.0062
9-13-12	12	.0138

From McHenry

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-19-00	36	.0091
9-26-12	16	-.0346

From Lewisburg

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
	NONE	

Table 7b. CHARACTERISTICS OF AIR PARCELS ARRIVING AT MCHENRY AFTER PASSING NEAR THE INDICATED OZONE MONITORING LOCATIONS.

From Coshocton

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-3-00	14	.0170
8-14-12	38	-.0008
8-16-00	20	.0150
8-30-12	36	.0136
9-3-12	40	-.0051
9-21-00	10	.0558
9-21-12	20	-.0270
9-24-12	14	.0309

From Kane

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-21-12	20	.0241
9-13-00	18	.1095
9-13-12	30	-.0124
9-15-12	30	.0209
9-30-12	16	

From McHenry

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-14-12	18	-.0058
9-14-00	38	.0258
9-20-00	12	.0745
9-21-12	12	-.0589

From Lewisburg

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
9-1-00	18	.1204
9-27-12	14	.0190

Table 7c. CHARACTERISTICS OF AIR PARCELS ARRIVING AT LEWISBURG AFTER PASSING NEAR THE INDICATED OZONE MONITORING LOCATIONS.

From Coshocton

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-5-12	38	-.0110
8-6-00	48	-.0034
8-16-12	26	.0102
8-21-12	18	.0809
8-29-12	22	.0241
9-11-12	48	.0016

From Kane

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
7-18-00	46	.0188
8-24-00	36	.1370
8-24-12	48	.0205

From McHenry

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-17-00	20	.0288
8-17-12	36	-.0016

From Lewisburg

Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-19-00	36	.0287
9-2-12	12	-.0534
9-17-12	18	-.0374

Table 7d. CHARACTERISTICS OF AIR PARCELS ARRIVING AT COSHOCTON AFTER PASSING NEAR THE INDICATED OZONE MONITORING LOCATIONS.

From Coshocton			From Kane		
Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})	Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
8-18-12	48	.0448	8-17-12	38	-.0172

From McHenry			From Lewisburg		
Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})	Arrival Time	Travel Time (hr)	d(lnC)/dt (hr^{-1})
	NONE			NONE	

progressively more rapid, beginning in the southwest and turning to a more westerly flow by the 28th. The rapid rise in ozone concentration at Coshocton is first apparent at 0000 GMT on August 27 when the wind flow has been from the west. The ozone continued to rise while Coshocton was in a 5 to 6 $m\ s^{-1}$ (10 to 12 kt) westerly flow, until August 28, 1200 GMT when the wind speed decreases to 3 $m\ s^{-1}$ or less. At Coshocton, the ozone concentrations decreased to near 160 $\mu g\ m^{-3}$ as the high center moved east. The trajectories clearly show the movement of the high pressure system and the return to a well defined anticyclonic flow over the entire area.

For the period following August 31, the trajectories show a slow southerly air flow from similar geographic areas at all locations. On September 1, the air arriving at McHenry and at Kane has previously passed over Lewisburg and over Coshocton, respectively. Table 7, a) and b), suggests that the air arriving at 0000 GMT showed an increase of concentration in transit (during the daytime) and a concentration decrease occurred during nighttime transit (arrival at 1200 GMT). These instances suggest that the diurnal trends of ozone production and destruction in the local environment may be a more predominant factor in the ozone changes that occur during transport from one location to another.

The cross-sectional analysis shows a decided warming of the high pressure center aloft and apparent subsidence of the air beginning about August 25. Although subsidence normally produces an inversion layer aloft, the subsidence inversion is not a persistent feature of the significant temperature analyses. The inversion appears at all four rawinsonde locations in late August, as the high pressure system is established, but it is conspicuously absent at all of the four locations in September. Twelve-hour ozone concentrations increased at Coshocton and McHenry during the time of subsidence, whereas the concentrations at Kane and Lewisburg were not substantially increased. After the subsidence ceased, the average concentrations at Coshocton began to decrease rapidly, remaining above 160 $\mu g\ m^{-3}$.

When the subsidence above 3 km at Pittsburgh stopped, the ozone concentration at McHenry continued to increase, before slowly decreasing. Once the subsidence ended at all altitudes and locations (about August 29), the lower 5 km of the atmosphere were only slightly stable (the isopleths of θ are widely spaced), a condition conducive to vertical mixing and dispersion; nevertheless, the ozone concentration remained quite high, day and night, at McHenry and near 160 $\mu g\ m^{-3}$ at the other locations.

During this episode, daily maximum temperatures at most locations in the study area were at or near their highest values for the summer. Through most of the daytime hours, skies were partly cloudy to clear. Usually, scattered high (cirriform) clouds persisted and scattered, fair weather cumulus clouds appeared during the day, but seldom did they cover more than four-tenths of the sky. This type of sky condition permits sustained solar radiation with few localized interruptions over the day producing high air temperatures. Also, the abundant sunshine should be conducive to ozone production.

During this episode of high ozone concentrations and high temperatures the mean water vapor mixing ratio of the mixed layer, R_{mix}, also reached and maintained its highest value. It exceeded 15.0 g kg^{-1}, at Pittsburgh, Dayton and Buffalo only during this episode. These magnitudes represent a departure of at least 1.6 standard deviations from the mean value of 9.8 g kg^{-1} for those three locations. Moisture content decreased from about 13 to about 7 g kg^{-1} in 24 hours as the front passed. Temperatures and ozone concentrations also decreased with the frontal passage.

There were 24 consecutive twelve-hour periods of high ozone at McHenry during late August and early September, a number that is three more than occurred during the remaining sampling times. The weather conditions, local and synoptic, that prevailed were unquestionably favorable for high ozone occurrences at McHenry. Those conditions are summarized as being characteristic of stagnant, warm core high pressure systems. Since the system stagnated for eleven days, almost centered at McHenry, the effects were most apparent there. Other locations were affected, to a lesser degree, i.e., presumably because the conditions were not optimal for continued high ozone concentrations.

9.0 FINDINGS AND CONCLUSIONS

Investigations of meteorological conditions which accompanied ozone concentrations during July through October at four nonurban locations were conducted. Linear relationships of those conditions with the longer term ozone concentrations were examined. Several avenues of approach were explored--trajectory analysis, pressure system intensities, cross-section analyses--which had not been used previously. Some of these avenues were fruitful and others were fruitless. Analyses of the data collected were conducted under four principal classifications. The results of those analyses are followed by the primary conclusions.

9.1 Fronts, Ozone and Potential Temperature Time Sections

- Large changes of ozone concentrations may be associated with disturbances in the lower atmosphere which extend above 2 km, but which are not necessarily associated with fronts;
- Relationships among fronts, ground level ozone concentrations, and the potential temperature time-sections were inconsistent between ozone monitoring locations, suggesting that local effects and situations are equally important to determining concentrations;
- The location of the ozone monitoring station with respect to local terrain and altitude may have a significant effect upon the daily range of ozone concentrations;
- Downward transport and diffusion of ozone from the stratosphere does not appear to account for occurrences of high ozone concentrations.

Therefore - *The major anomalies in the vertical structure of the lower troposphere are important to the occurrences of high ozone concentrations.*

9.2 Air Parcel Trajectories

- High ozone concentrations are usually associated with slower moving air, whereas the low ozone concentrations are usually associated with faster air movement;
- No single region of the northeastern United States is implicated, by trajectory analysis, as the source of the observed high ozone concentration;
- High and low ozone concentrations may be associated with trajectories passing over nonurban areas as well as urban areas;

- Low ozone concentrations may be associated with trajectories passing over urbanized areas.

Therefore - *The path which the air takes enroute to the four ozone monitoring locations influences, but does not determine, the measured ozone concentration.*

9.3 Mixed Layer Properties

- Of the variables tested, the mean water vapor mixing ratio has the greatest statistical relation to the twelve-hour average ozone concentrations.
- The poo correlation of the percentage rate of change of ozone concentration at McHenry with the water vapor mixing ratio suggests that the generation of ozone is not dependent upon the amount of water vapor present.
- The positive correlation of ozone concentration and the water vapor mixing ratio precludes the descent of ozone from the stratosphere as an explanation of the high ozone concentration at the ground.
- The ozone concentration has little relationship to the currently observed wind vector.

Therefore - *Measurements of the moisture content of the air should be made with all ozone studies, until or unless experimental evidence directs otherwise.*

9.4 Maximum Temperature and Maximum Ozone Concentration

- Ozone concentrations in excess of NAAQS did not occur on days when the maximum temperature was less than 16.5°C.
- Ozone concentrations tend to increase as the daily maximum temperature increases.

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APPENDIX A

BASIC DISCUSSION OF POTENTIAL TEMPERATURE ANALYSIS TECHNIQUES

Potential temperature is an ideal quantity to examine the static and dynamic processes of the lower troposphere. Designated by θ, it equals the temperature that a parcel of air would have if the parcel were brought to a pressure of 1000 mb without exchanging heat energy with the environment. The First Law of Thermodynamics shows that as air ascends or descends without exchanging heat (an adiabatic process), θ is unchanged (conserved). Thus, θ is a measure of the thermodynamic energy potential of dry air. Within an air parcel, changes of θ occur through energy input or extraction. Nocturnal radiational cooling, daytime solar heating, and condensation/evaporation of moisture are the primary ways of changing θ in a moving parcel of air. In the absence of phase changes of water, the primary effect of diabatic heating (changing θ), is confined to the near-ground layers (below 1 to 2 km) of the atmosphere where the diurnal radiative heating and cooling cycle occurs.

Vertical Distribution and Stability

Normally, θ increases with increasing altitude. The vertical gradient of θ, $\frac{\partial\theta}{\partial z}$, is related to the vertical temperature gradient, $\frac{\partial T}{\partial z}$, by

$$\frac{1}{\theta}\frac{\partial\theta}{\partial z} = \frac{1}{T}\left(\frac{\partial T}{\partial z} + \Gamma\right)$$

where

$$\Gamma = 9.8^\circ\mathrm{K\ km}^{-1}$$

is the adiabatic temperature gradient. When the pressure is approximately 1000 mb (~100m MSL), $T \sim \theta$ and $\frac{\partial\theta}{\partial z} \simeq \frac{\partial T}{\partial z} + \Gamma$. Thus, unless $\frac{\partial T}{\partial z}$ is less than $-\Gamma$, θ will increase with altitude.

When an air parcel is lifted adiabatically from one altitude to another, the air at the higher altitude will usually have a higher θ. The lifted parcel must acquire heat energy in order to be in equilibrium with the new environment, or it will return to its original energy level, i.e., the air parcel is stable (not buoyant) with respect to vertical displacement when $\frac{\partial\theta}{\partial z} > 0$. Using the same scenario for the condition, $\frac{\partial\theta}{\partial z} = 0$ ($\frac{\partial T}{\partial z} = -\Gamma$ near the ground), reveals that the vertical displacement is neutral--neither stable or unstable--and, when $\frac{\partial\theta}{\partial z} < 0$ ($\frac{\partial T}{\partial z} < -\Gamma$ near the ground), vertical displacements are buoyant in an unstable, superadiabatic state.

Inversion layers where $\frac{\partial T}{\partial z} \geq 0$ are very stable with respect to vertical motion because θ increases very rapidly with altitude. The inversion layers may be only a few tens of meters thick, or a few hundred meters thick. The potential temperature changes across the inversion, not its thickness, measures the intensity of the inversion. A very strong inversion may occur within a short distance, and a weaker inversion over a greater depth. The presence of an inversion can best be seen when the analysis interval is small enough (~ 1 0 K or 0.5 K) to show details.

When air aloft descends (subsidence occurs) condensation does not occur and radiative heat gains or losses are quite small, resulting in an adiabatic process. A subsiding air parcel that has a θ value at an initial time and altitude will be found at a lower altitude, with the same θ at a later time. During that time period, θ will have increased at the initial and the lower altitude. Subsidence stabilizes the air, often forming inversion layers.

Time-Altitude Sections

In a time-altitude section of potential temperature, the viewer is thought of as standing in one place, watching the air in a vertical column of fixed height move past. The distribution of isopleths of θ with altitude and time show the changes which take place in the air.

If there were no transitory systems, the air above the heat-cooling layer would remain stratified with little change in time or altitude in the vertical distribution of atmospheric variables, including θ. Then isopleths of θ in the time-altitude section would be horizontal. When events occur to change the distribution of θ, the structure of the atmosphere is changed because atmospheric energy is redistributed and dynamic processes are at work changing other properties, perhaps including atmospheric ozone.

For a given altitude, above surface heating influences, an increase of θ with time indicates a warming of the air, resulting from the horizontal advection of warm air from upstream and/or the descent of air from a higher altitude. Isopleths of θ slope toward lower altitudes as time increases. Conversely, a decrease of θ might be associated with cold air advection and/or uplifting of air. In either of those cases, isopleths slope toward higher altitudes (upward) as time increases.

Major cooling of the air would probably be associated with cold fronts passing the sounding station. The fronts are followed by gradual warming. The greater the contrast of θ across the front, aloft and at the ground, the greater the intensity of the front and the greater the contrasts of the air masses. The stronger fronts exhibit frontal characteristics (have greater changes of θ with time) to greater depth of the atmosphere. So, θ time sections reveal frontal intensity and depth.

Major warming could arise from passing warm fronts, but they are weak and rare in the study area during the summer. Large-scale subsidence is the remaining mechanism for a major warming of the air, i.e., increasing θ at a given altitude. If the warming occurs over a wide area, it could only be in conjunction with a high pressure system. The individual time sections of θ from rawinsonde locations in the affected area should show θ isopleths decreasing in altitude as time increased. The slope of the isopleth is indicative of the magnitude of the subsidence rate.

Other basic discussions of potential temperature and cross section analyses are found in General Meteorology by H. R. Byers, or Principles of Meteorological Analysis, by W. J. Saucier.

APPENDIX B

AIR PARCEL TRAJECTORIES
AT
900 mb

July 4 to October 31, 1973

for Air Arriving at

McHenry, Maryland
Kane, Pennsylvania
Coshocton, Ohio
Lewisburg, West Virginia

Air parcel positions at twelve-hour intervals prior to arrival are indicated by a triangle (Δ) for those air parcels arriving at 0000 GMT and by a square (□) for those arriving at 1200 GMT. Month and day are indicated in the lower left corner of each panel.

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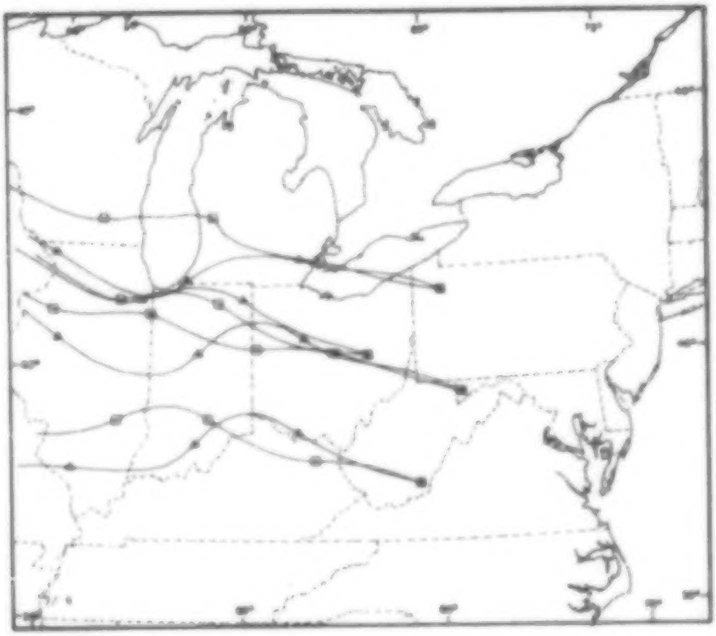

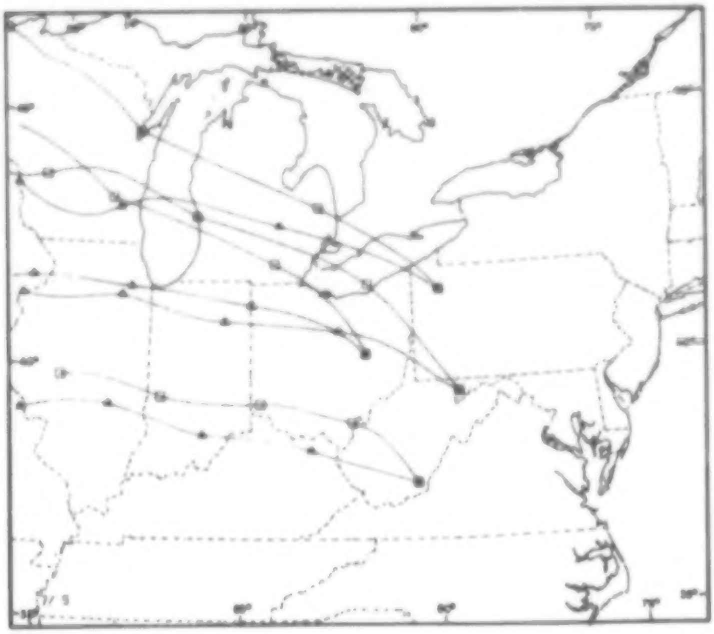

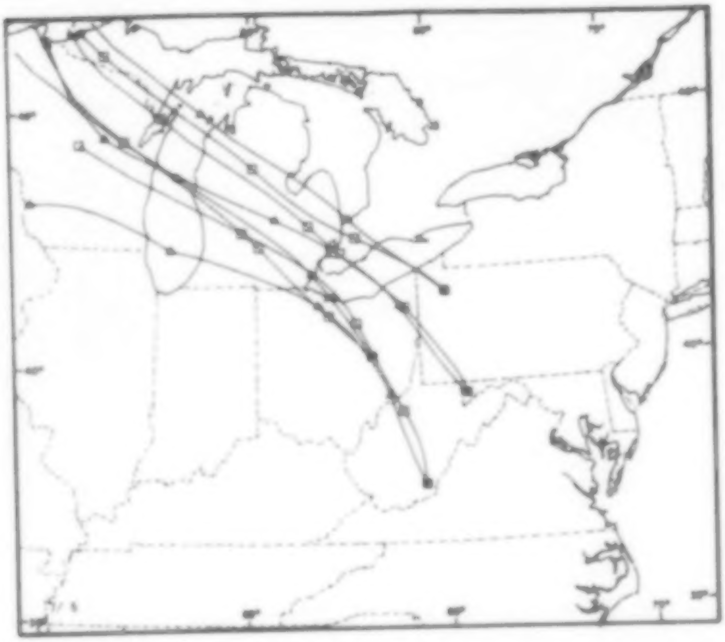

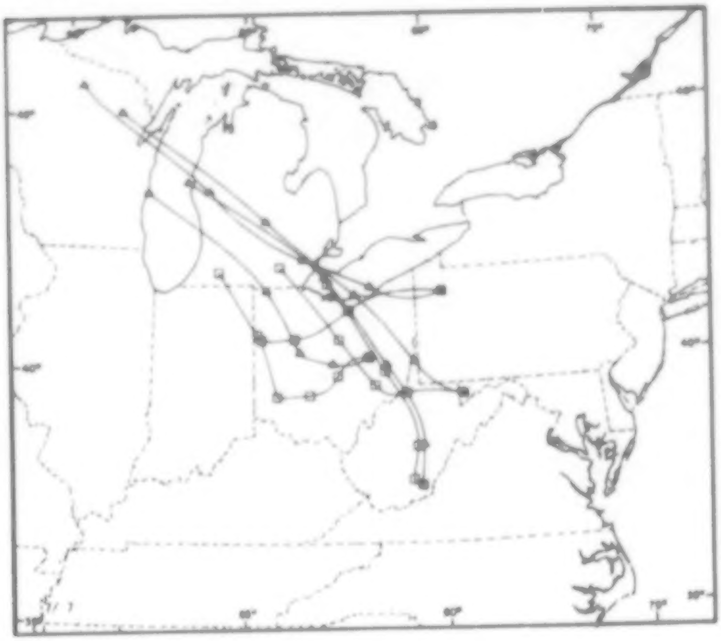

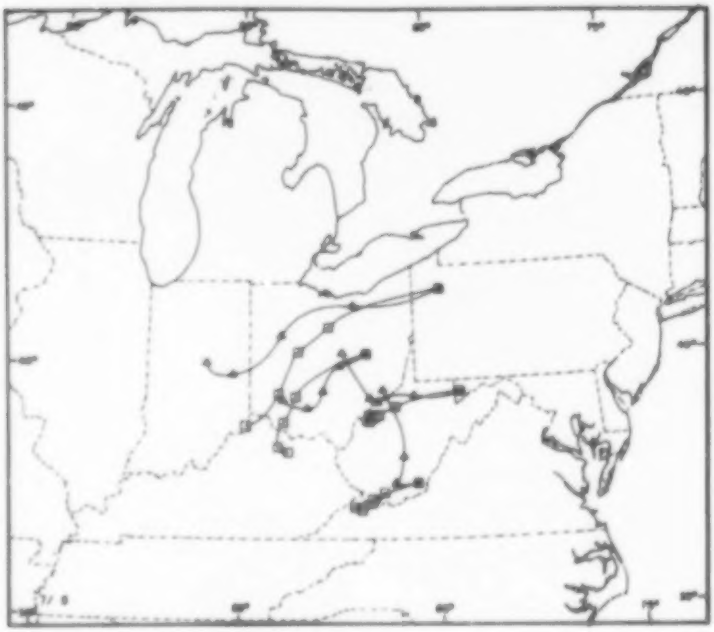
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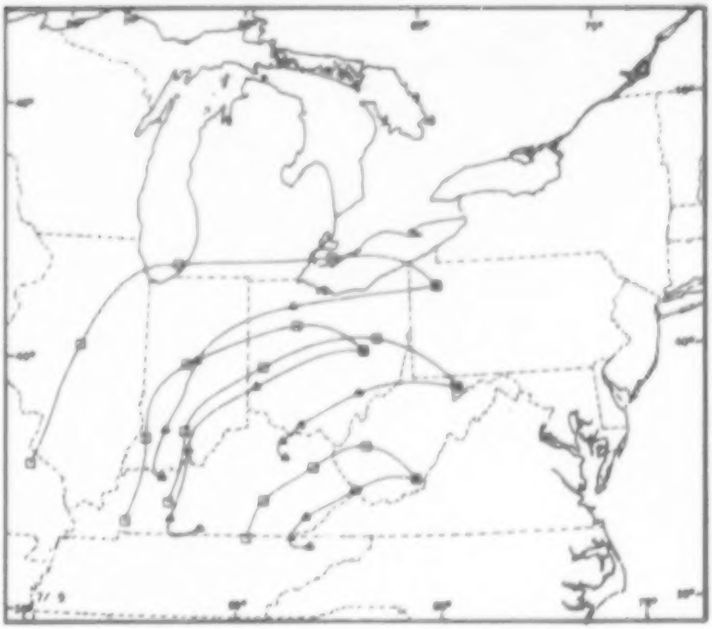
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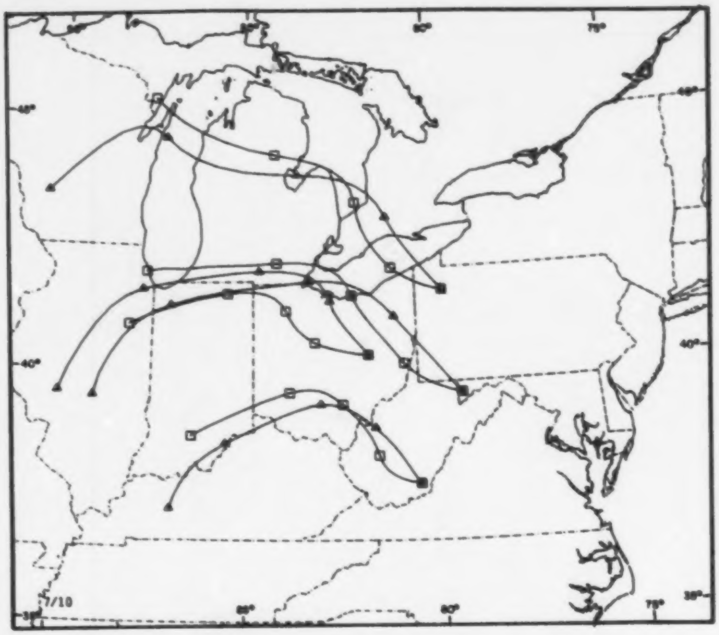
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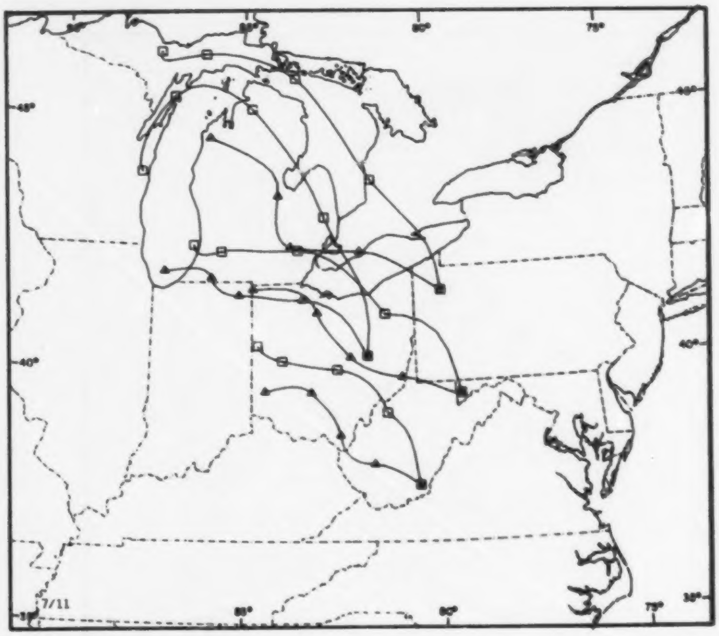
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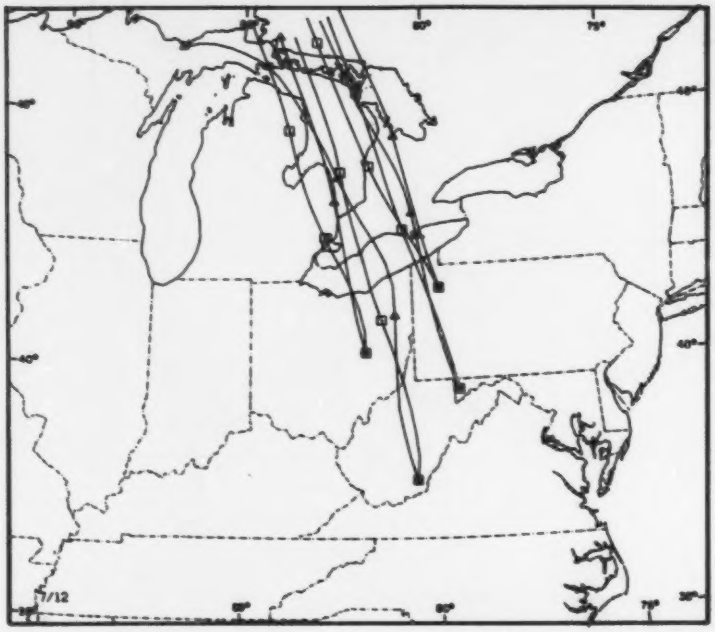
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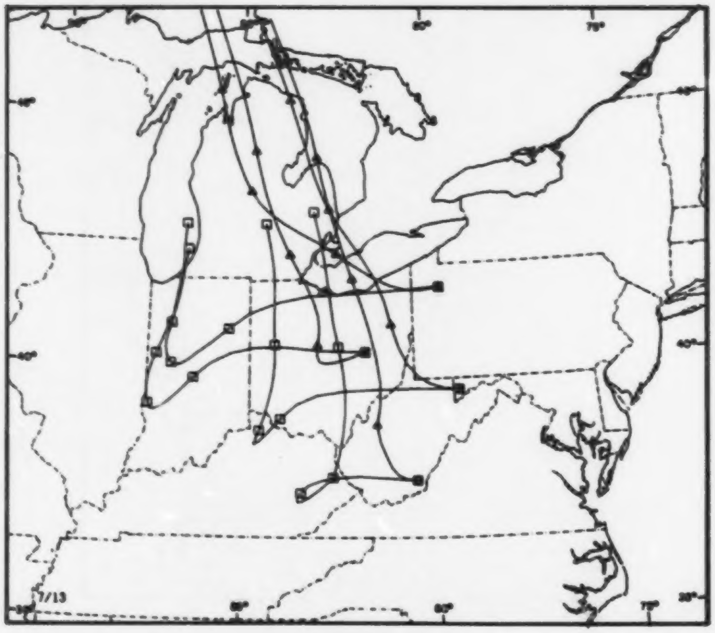
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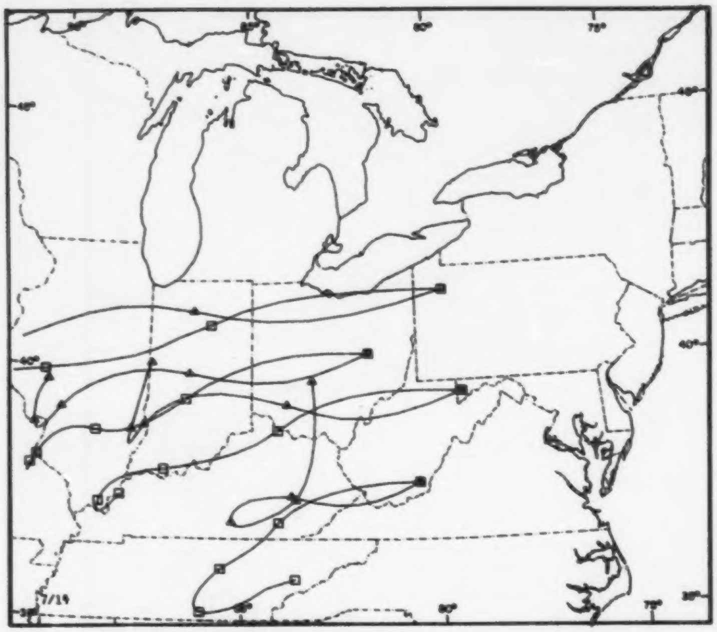
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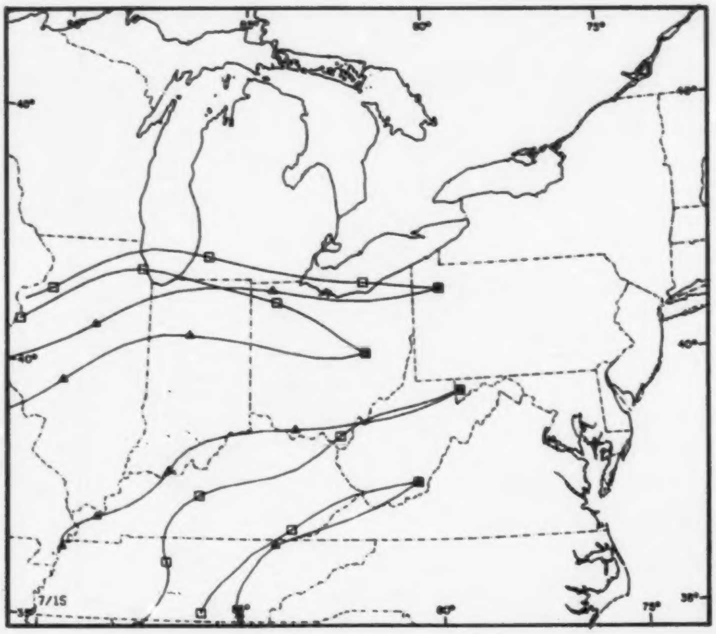
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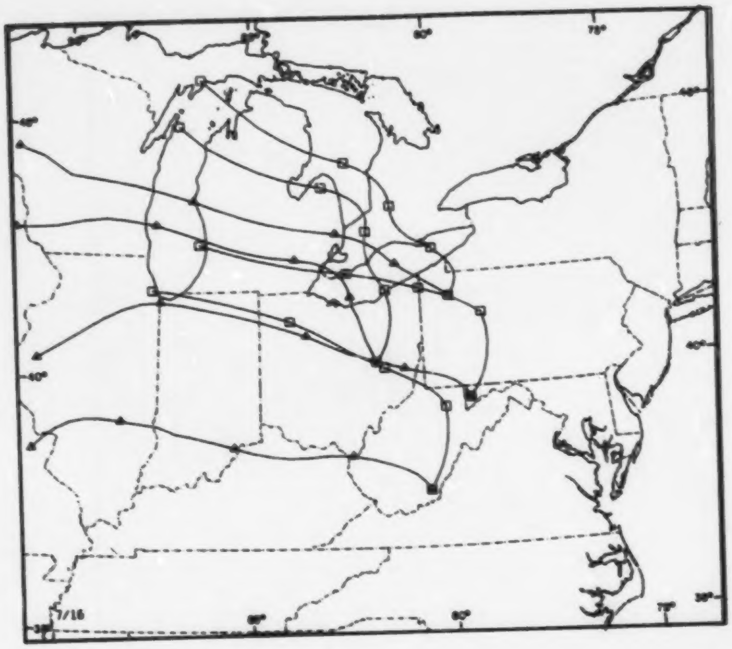
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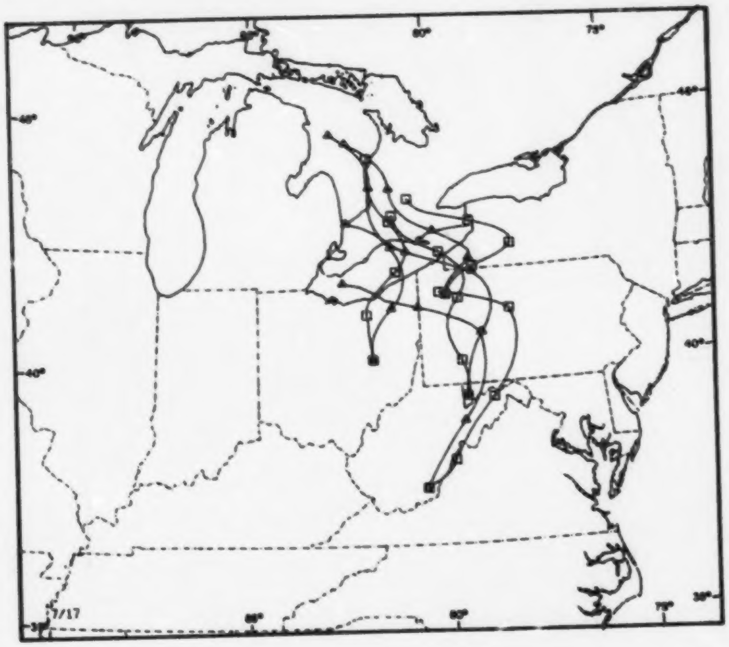
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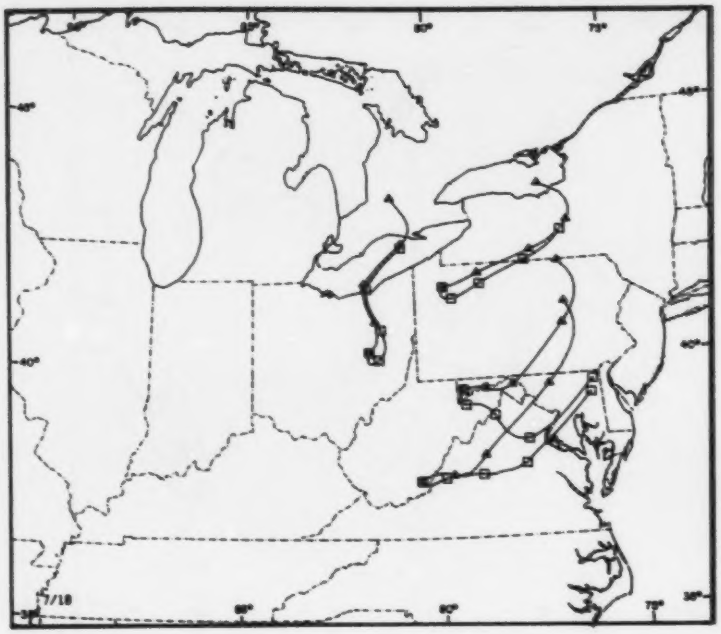
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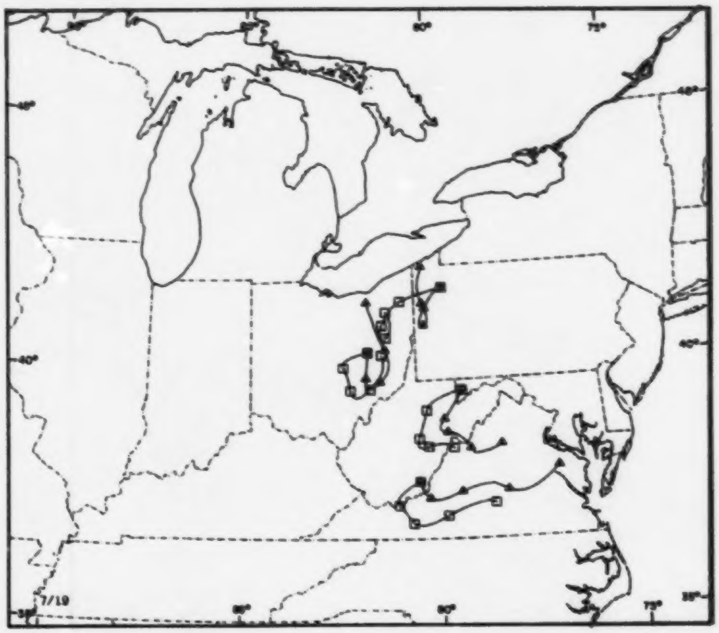
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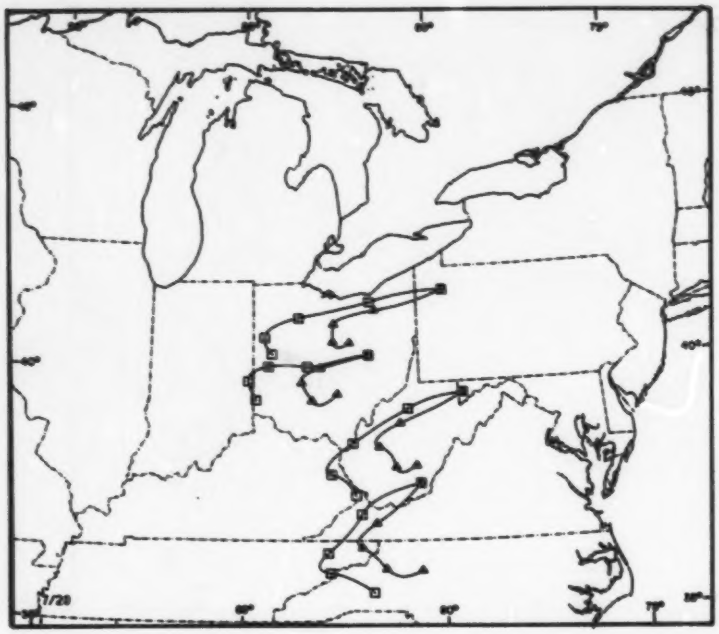
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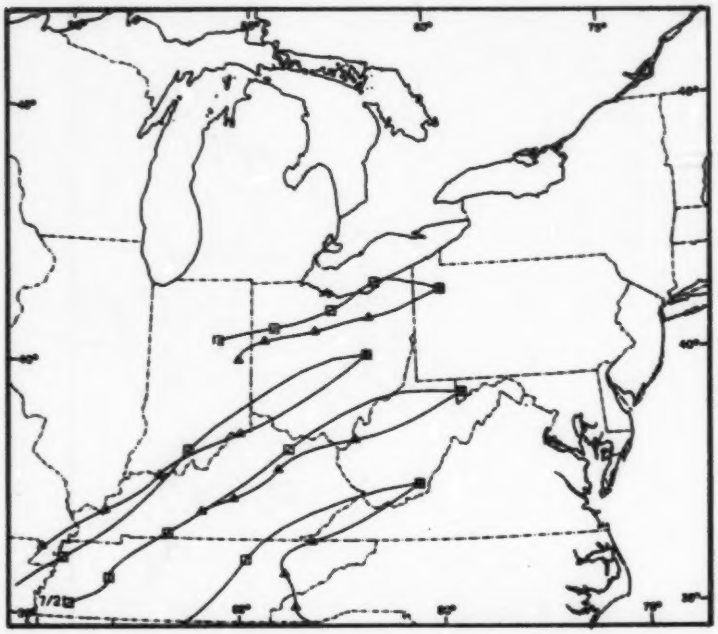
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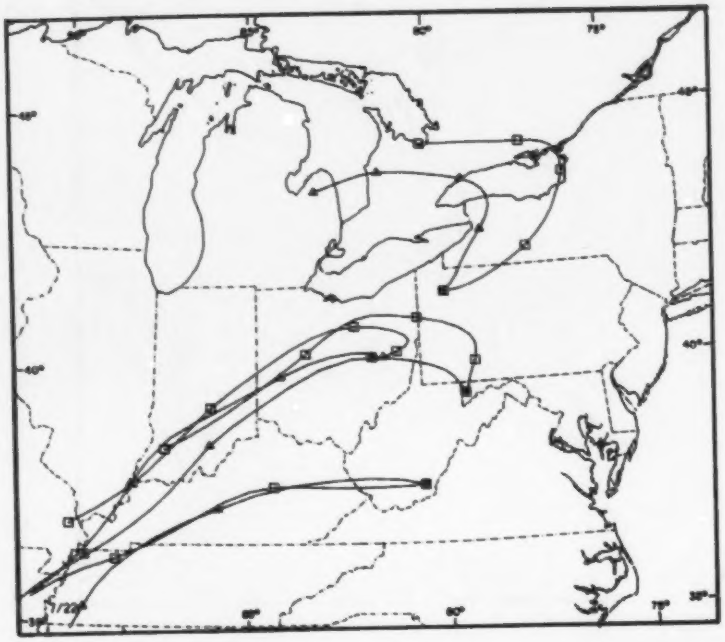

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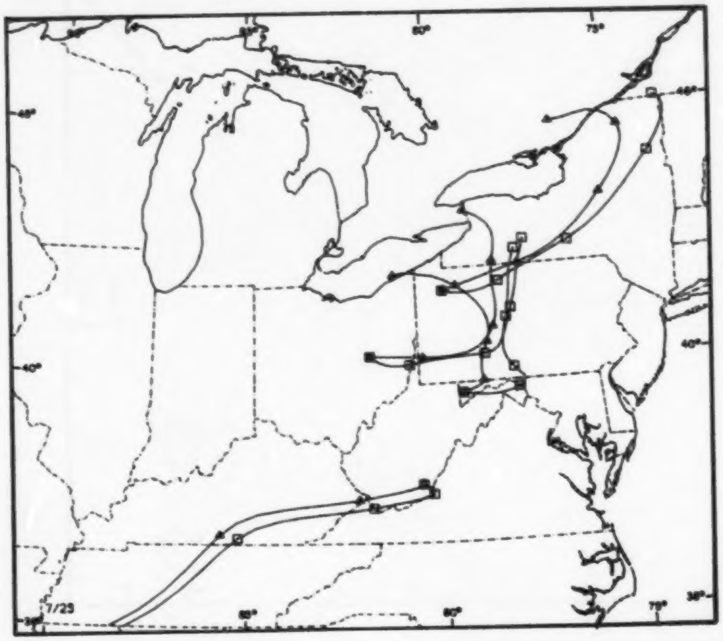

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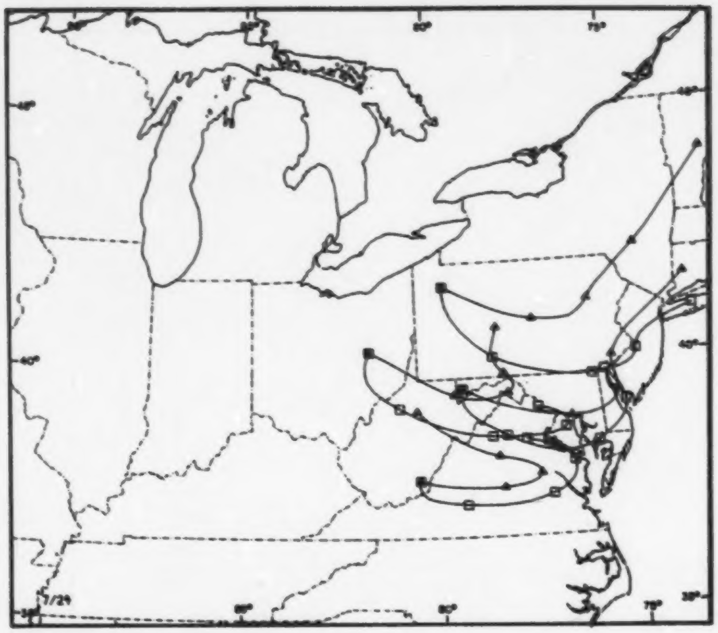

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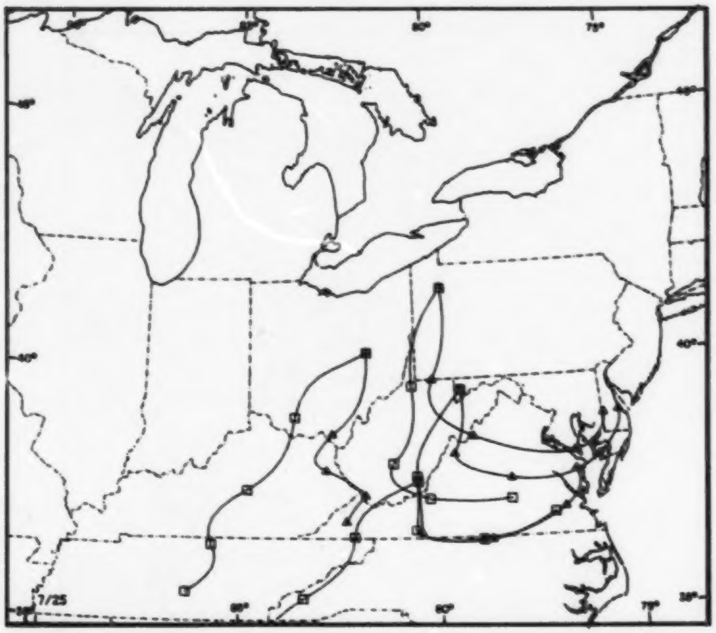

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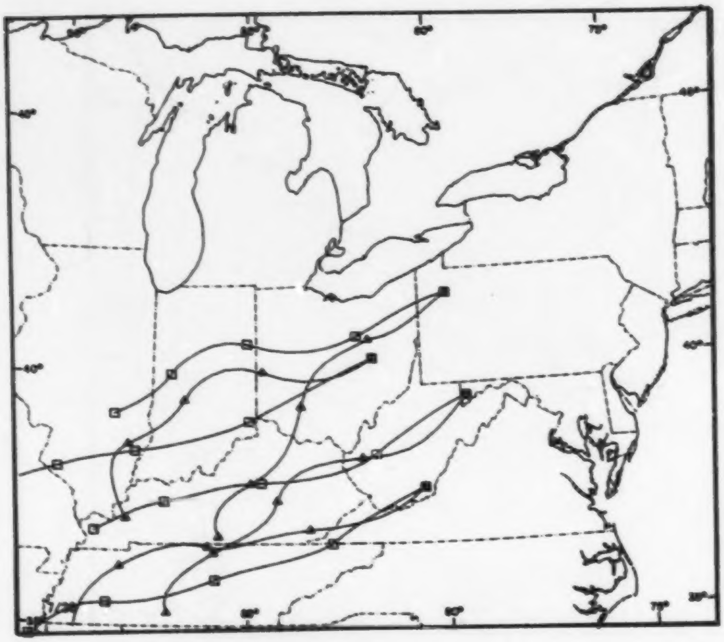
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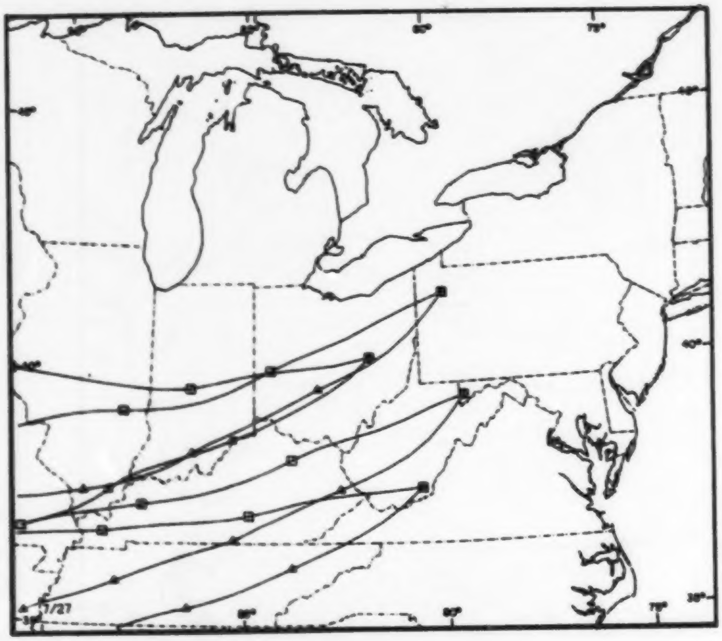
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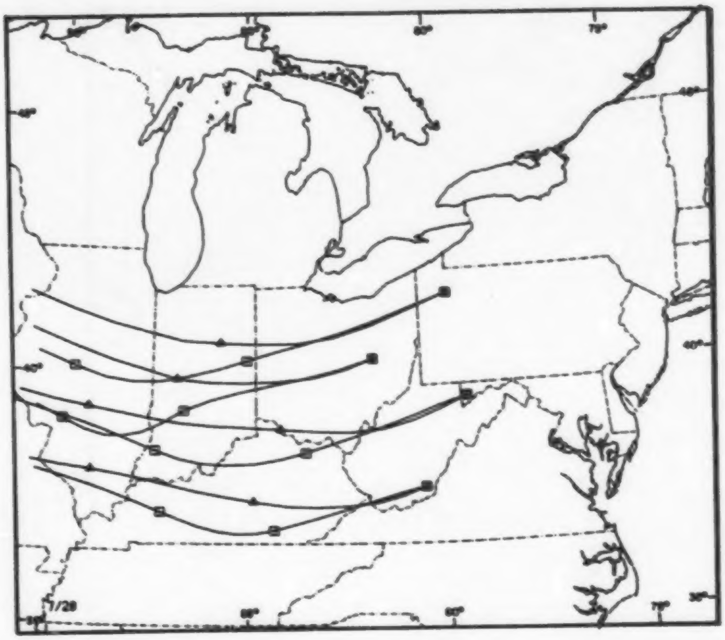

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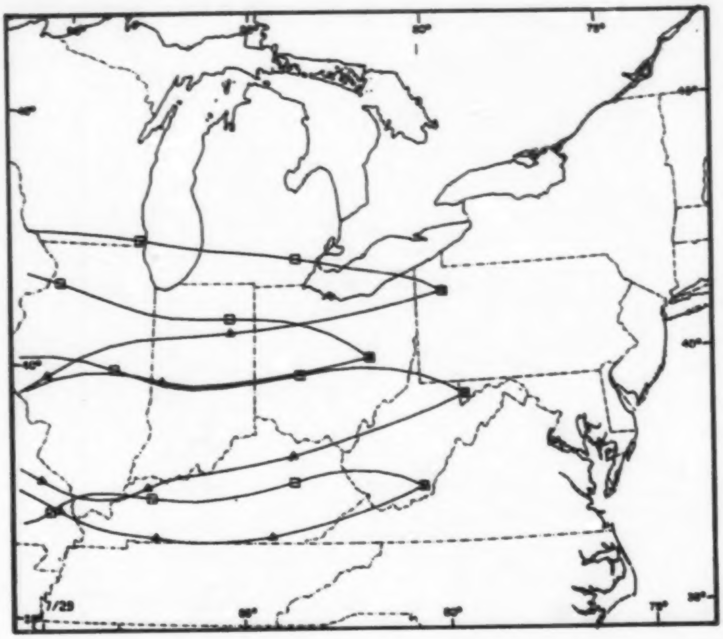

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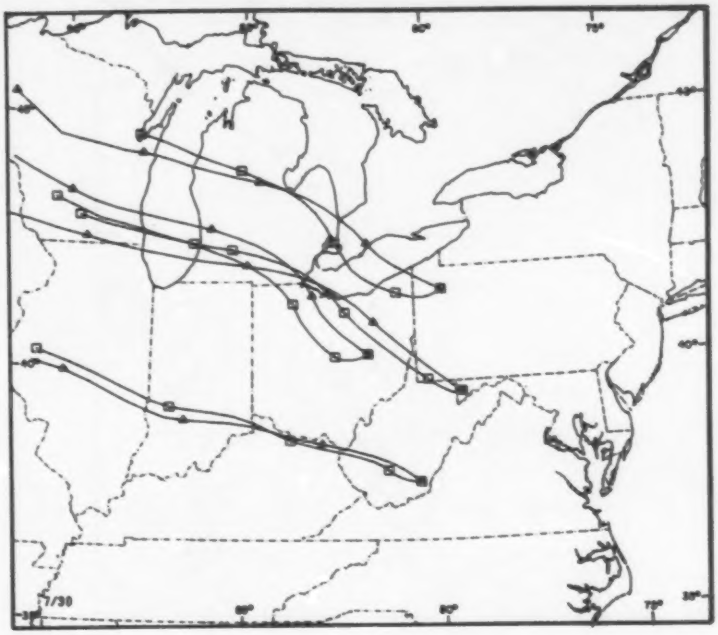
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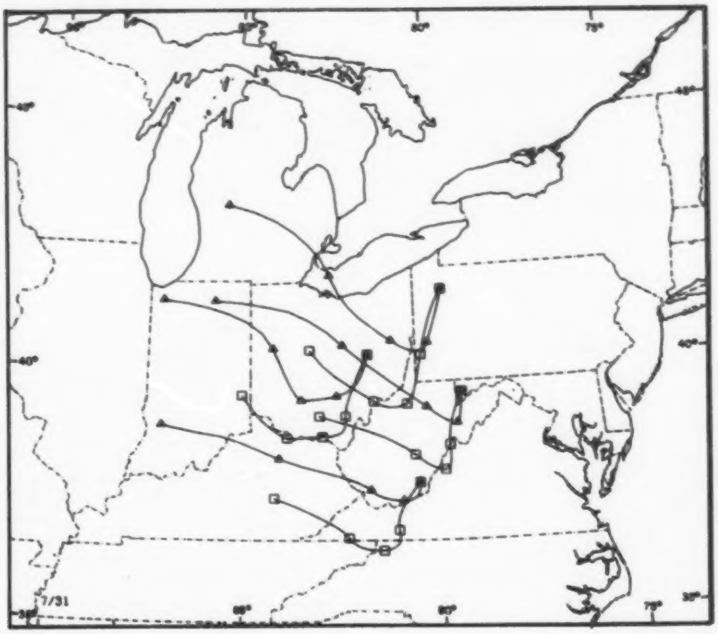
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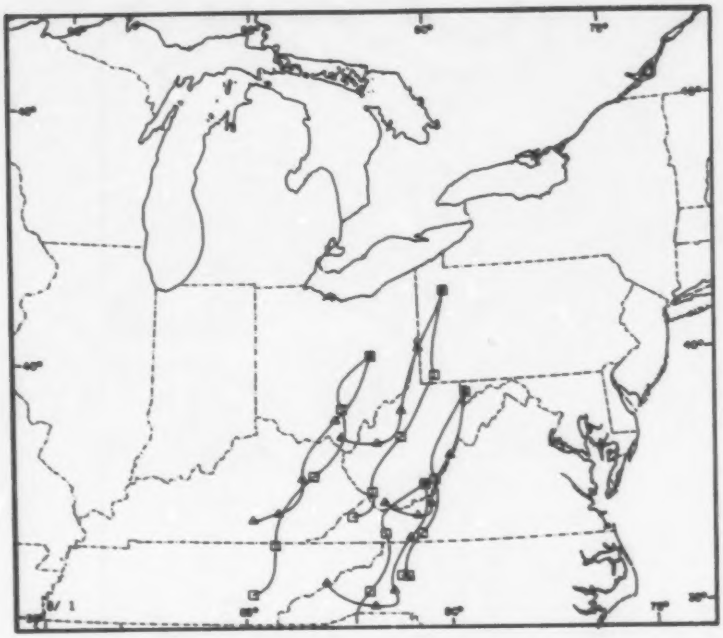

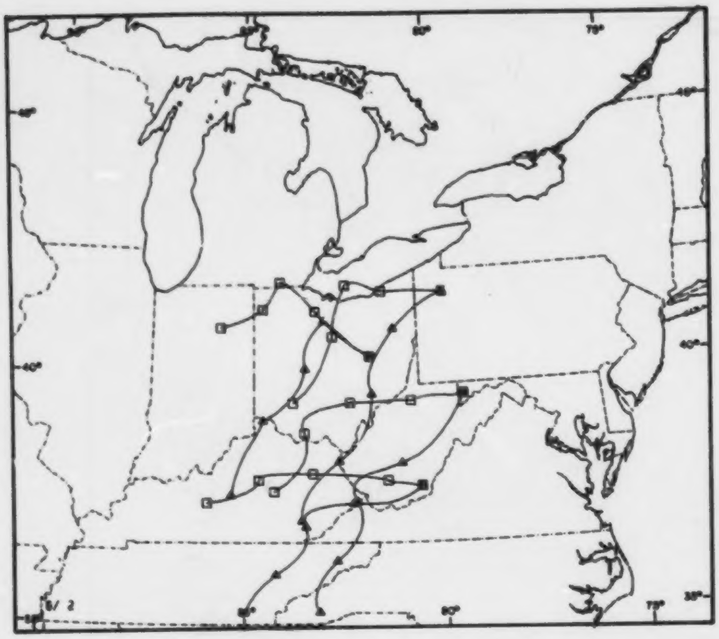
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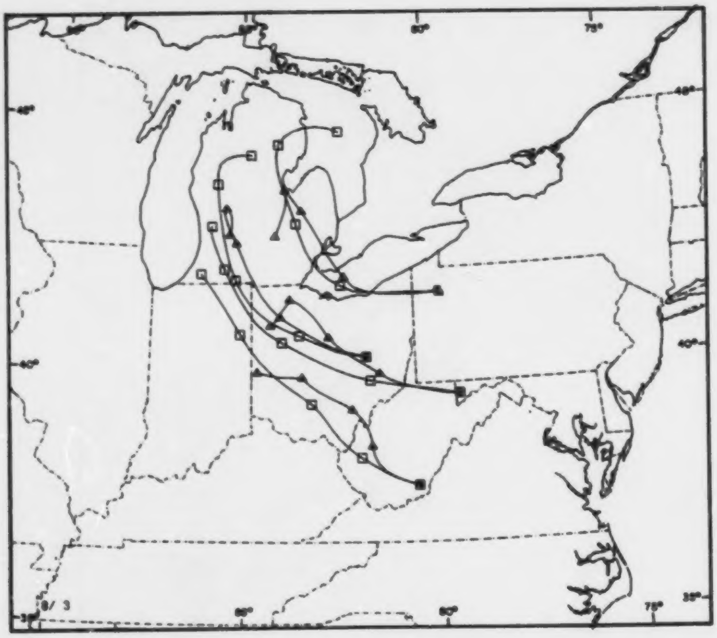
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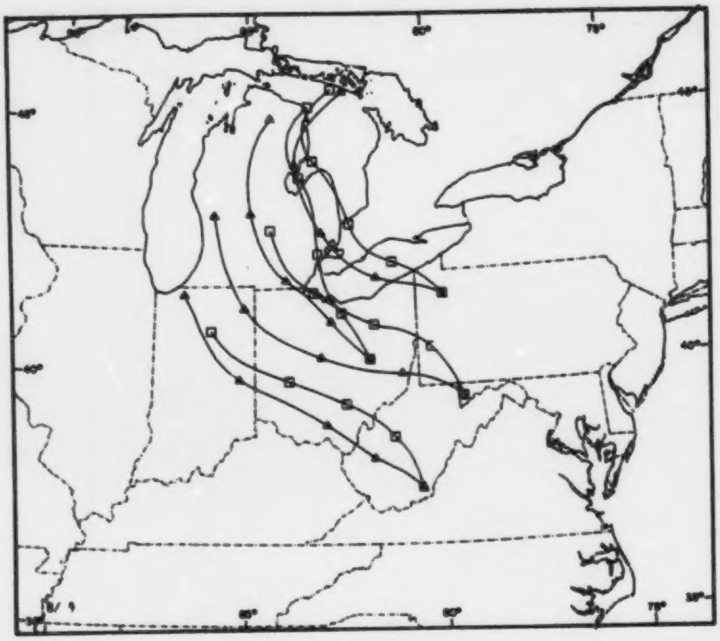
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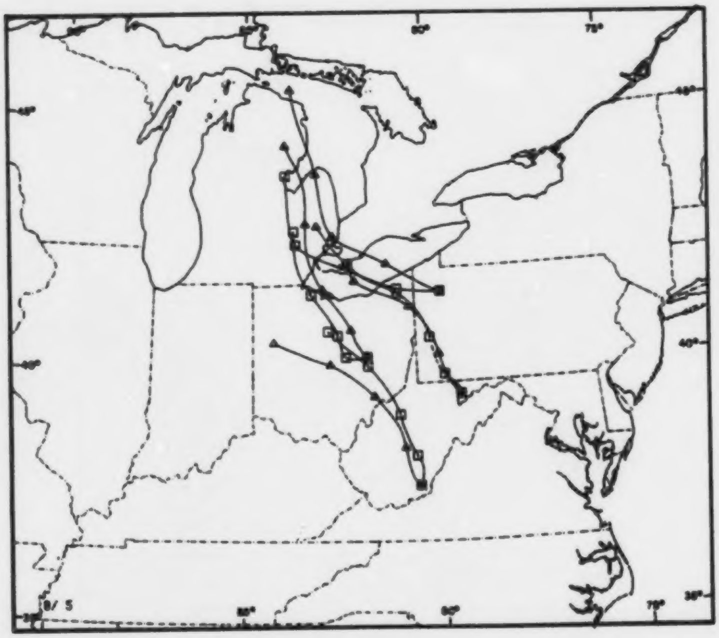
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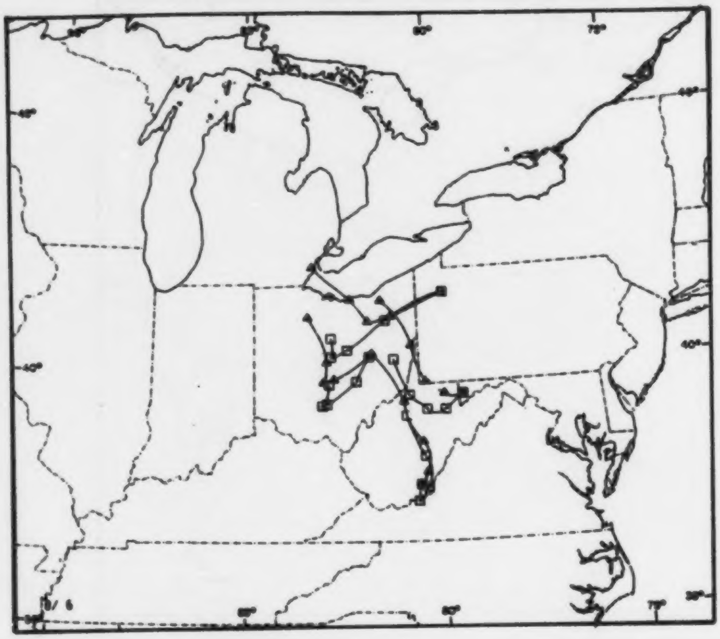
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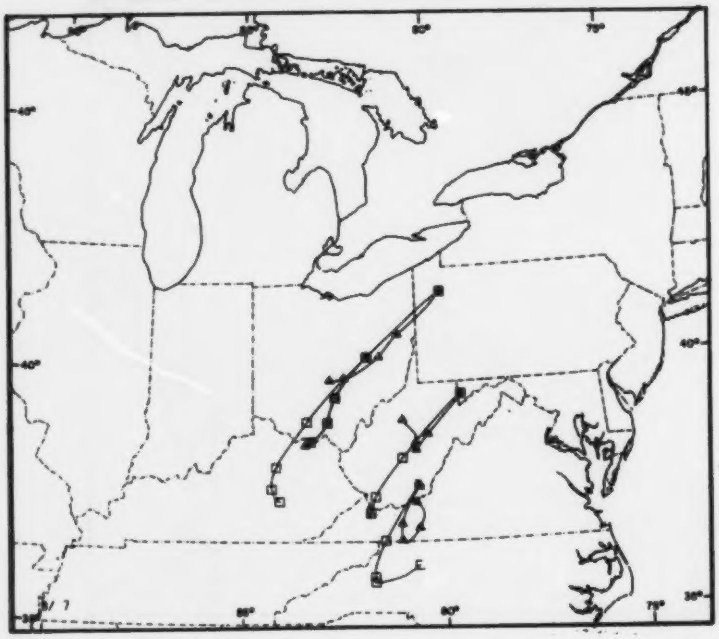
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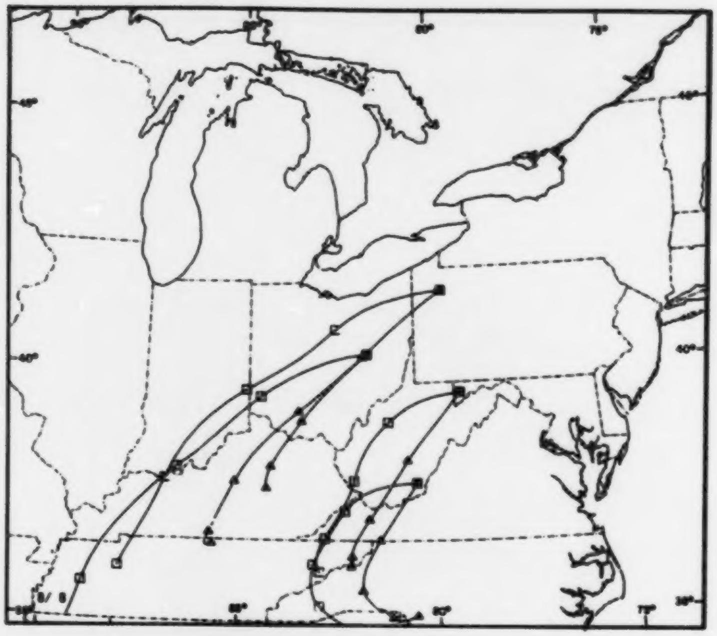
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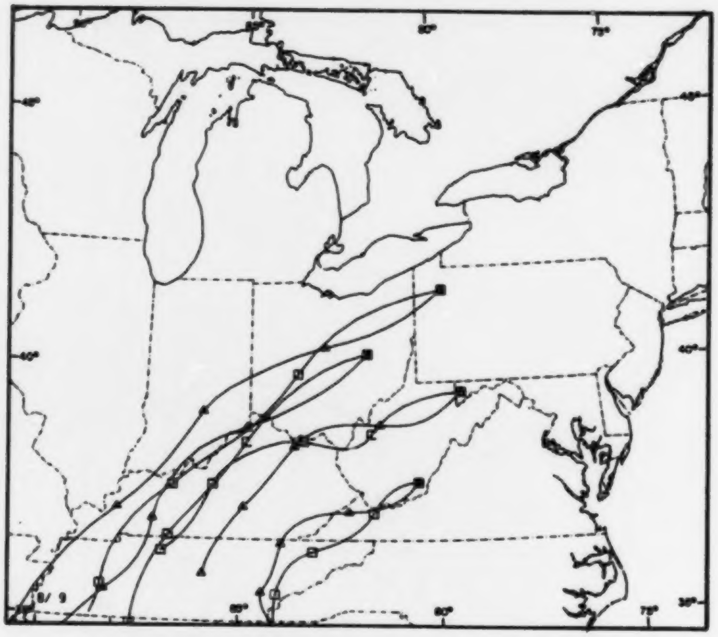
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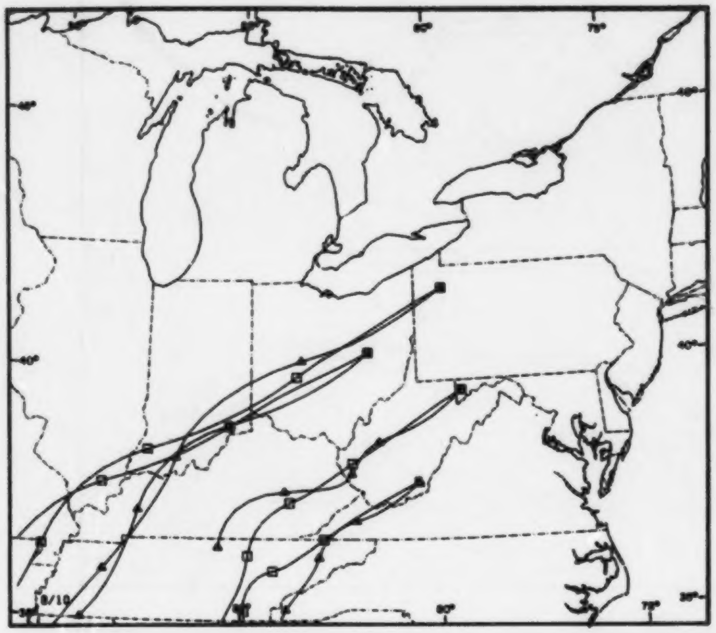
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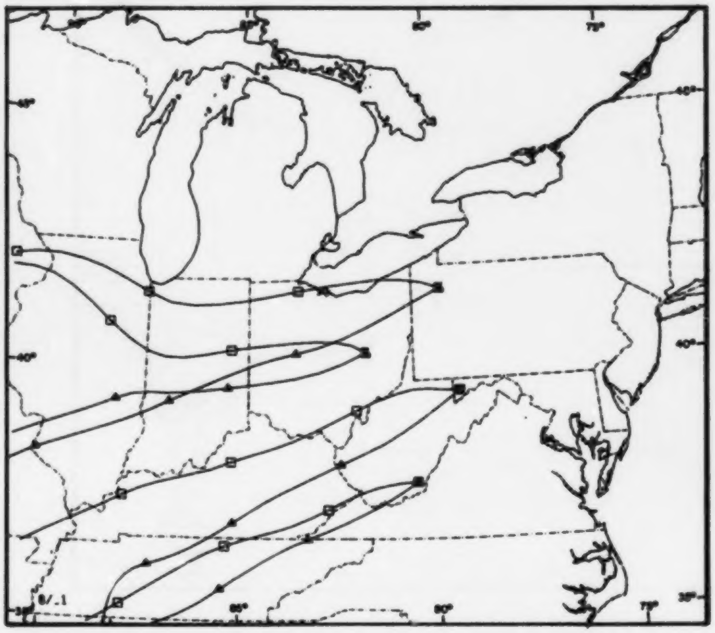
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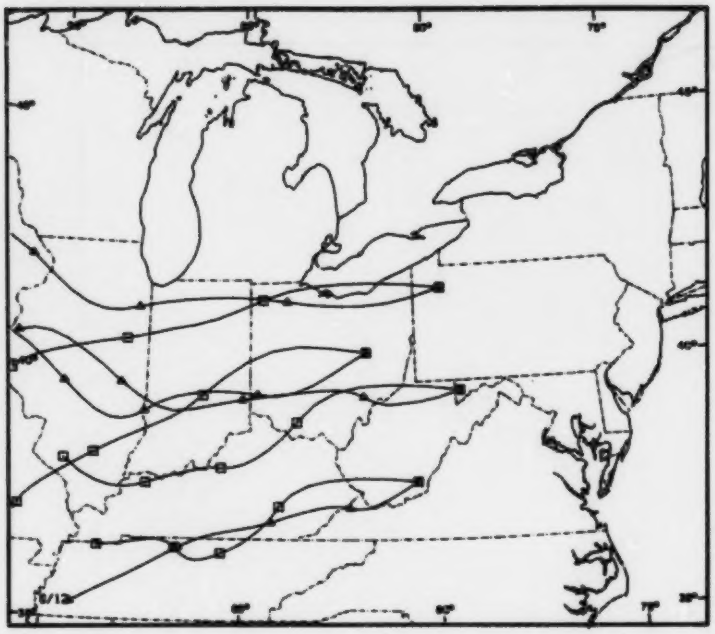

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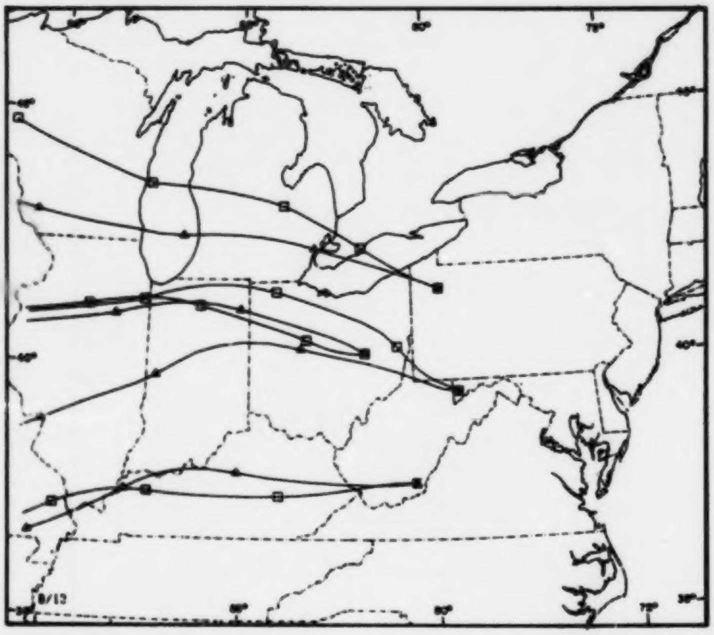

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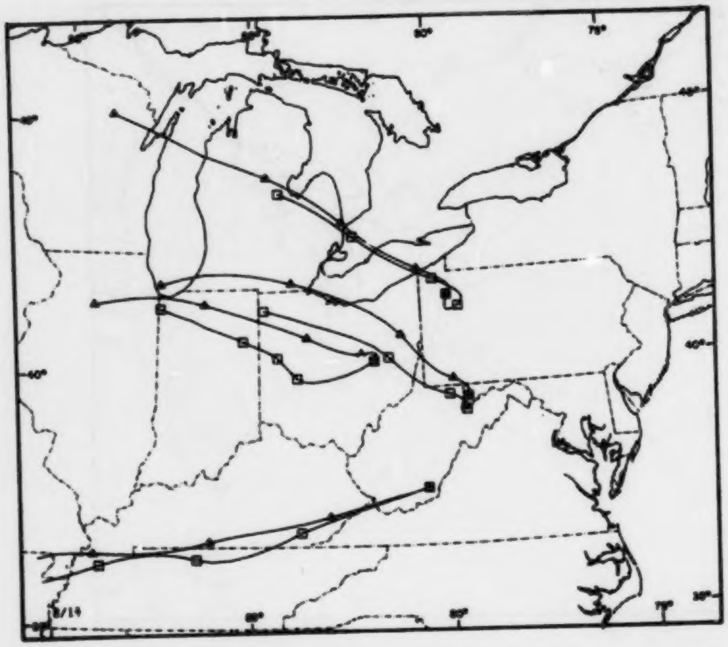
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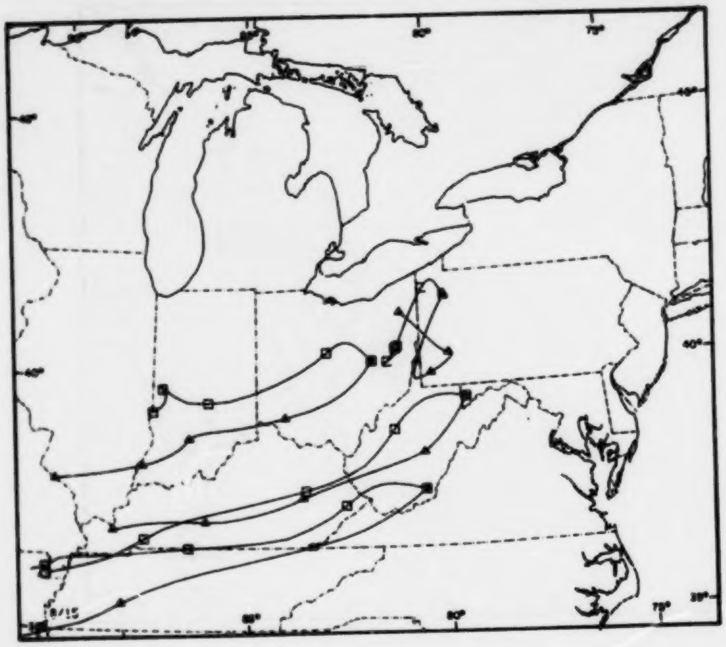
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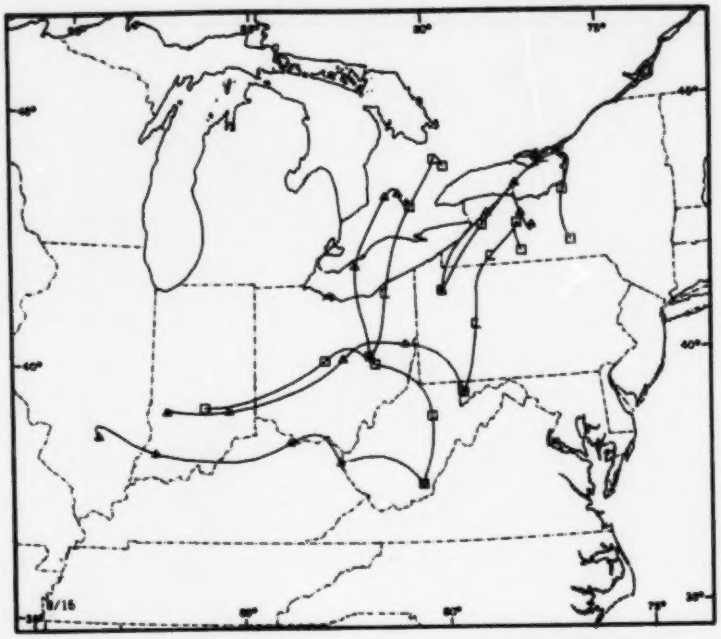
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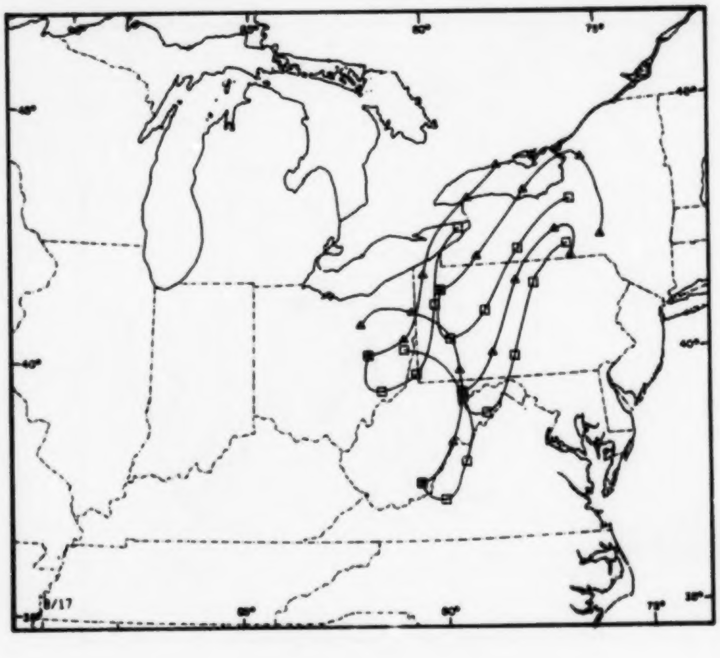
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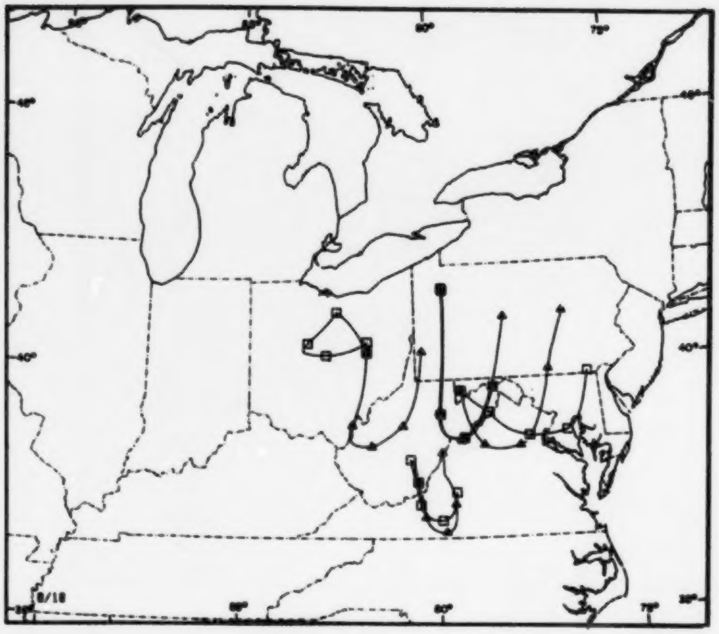
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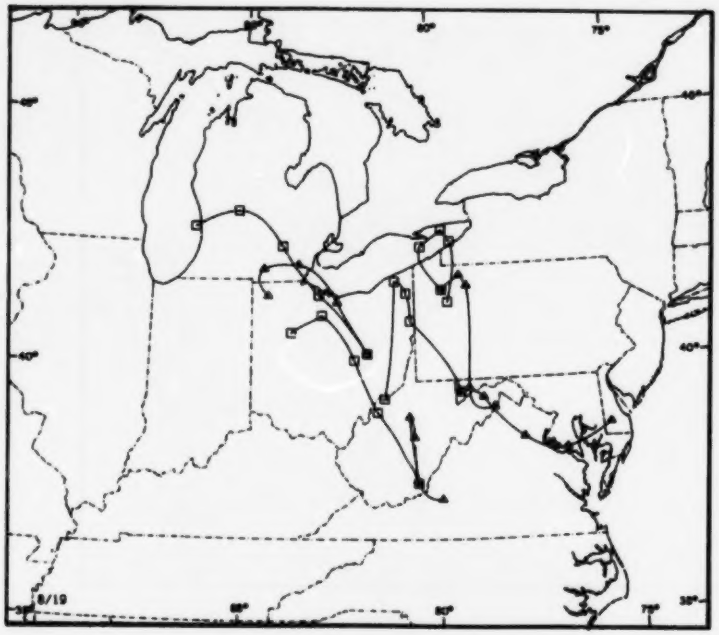
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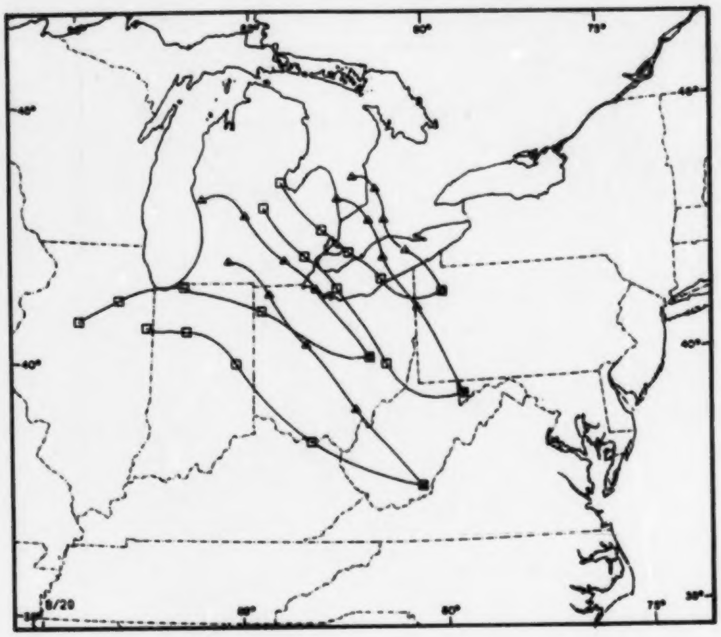

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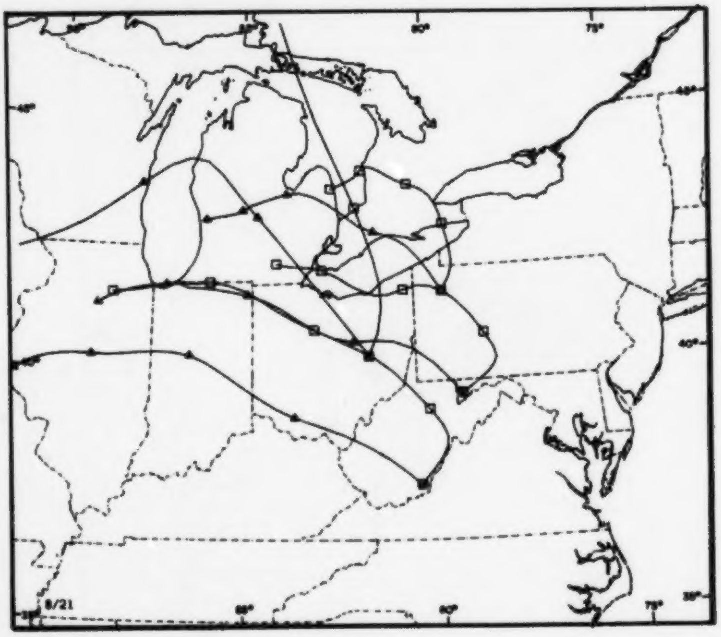

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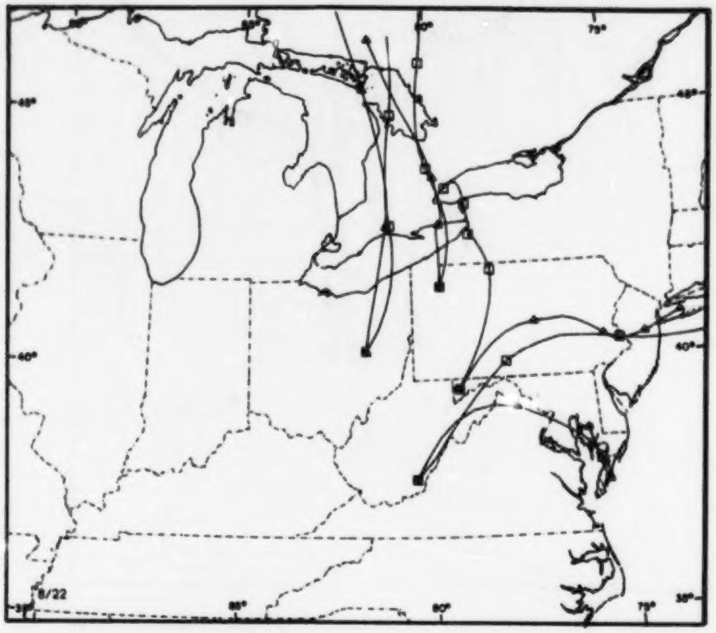
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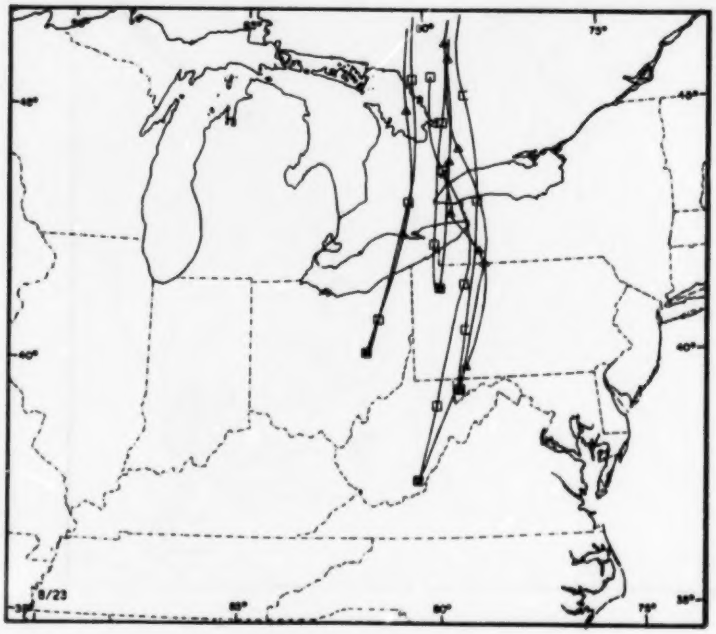
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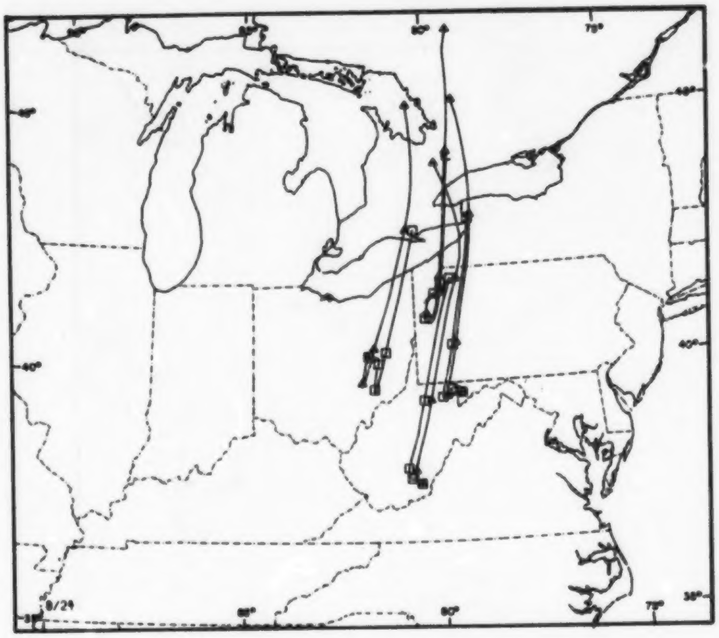
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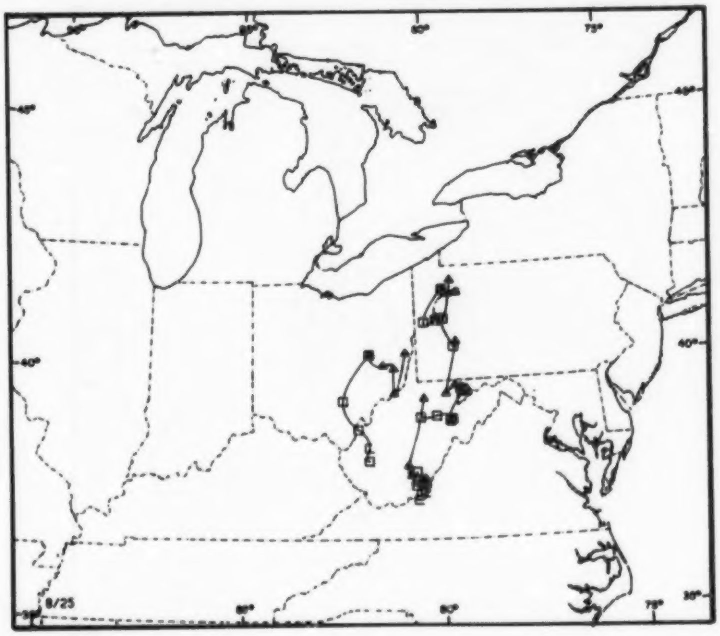
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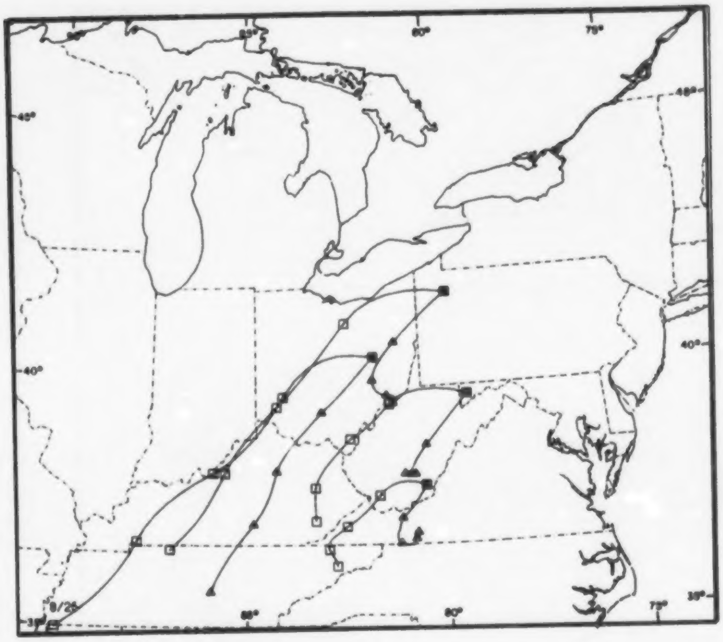
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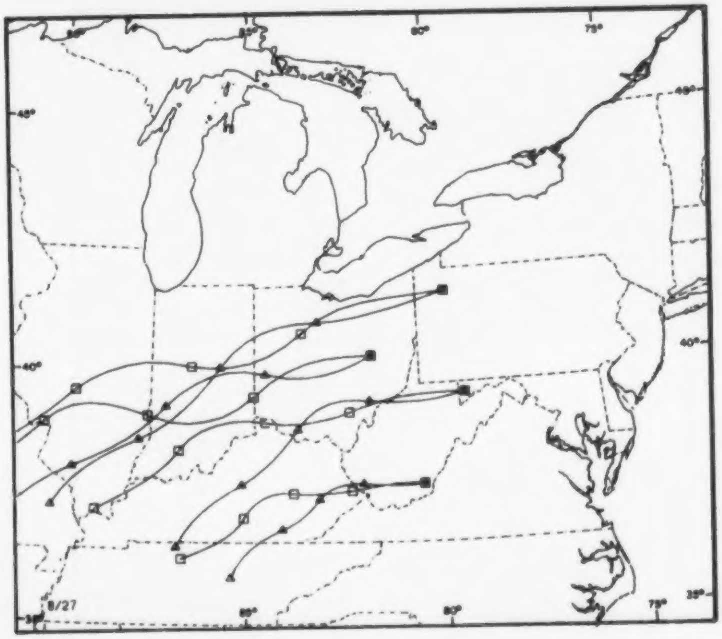
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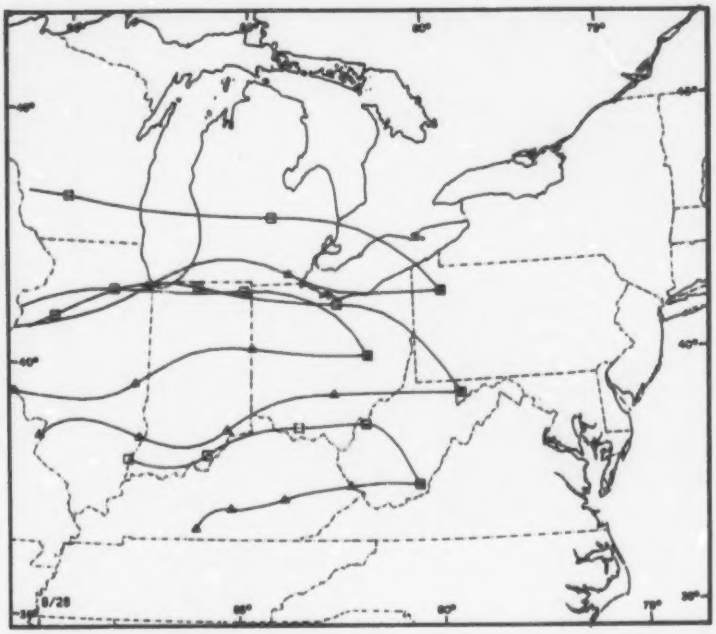
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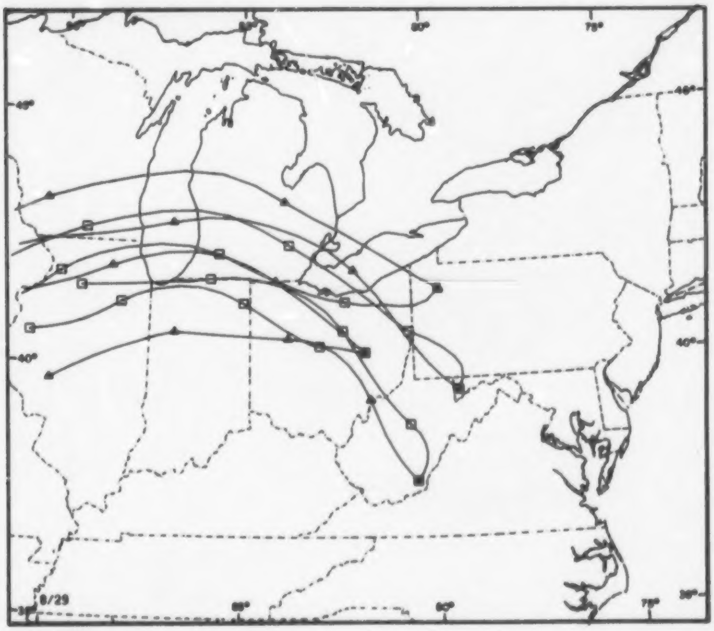
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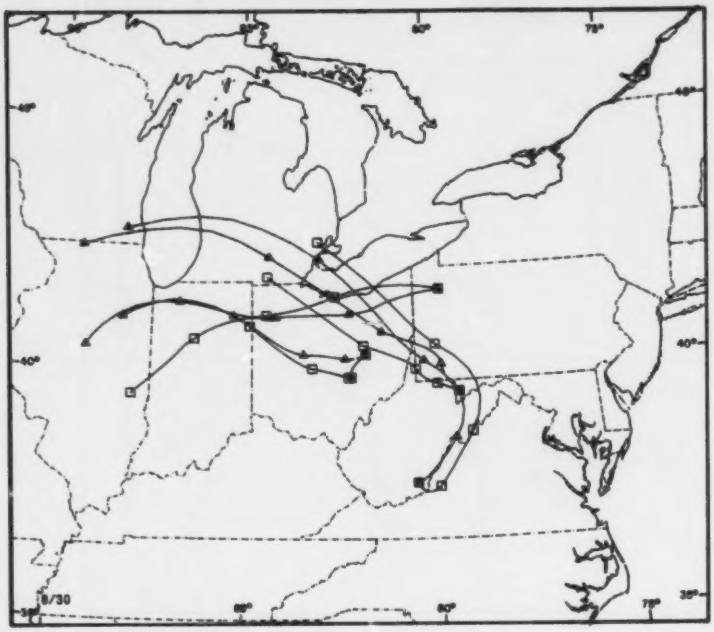
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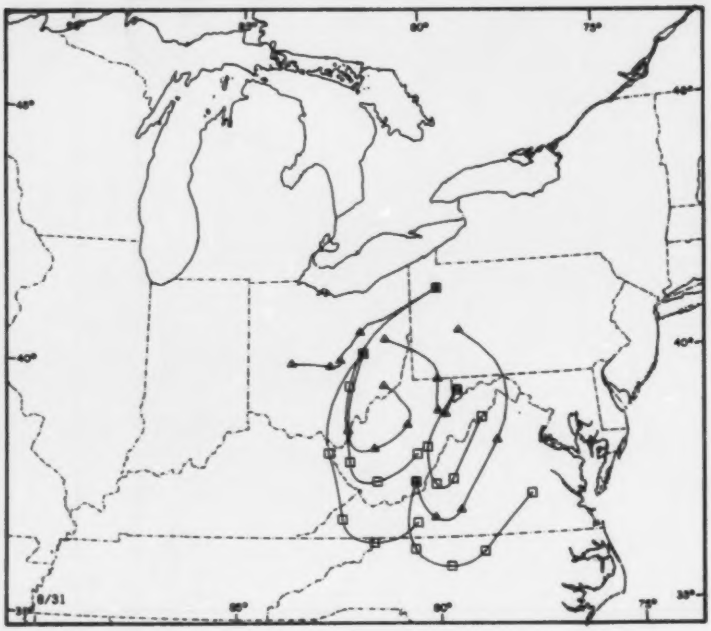
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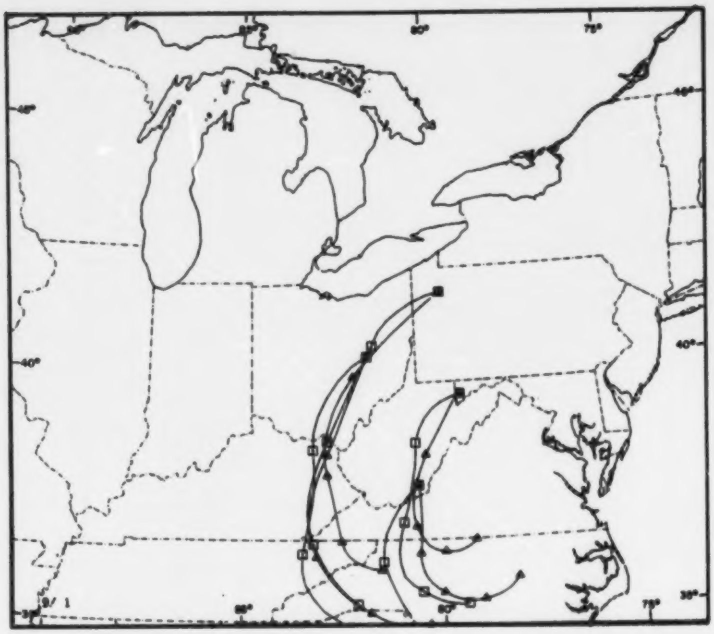
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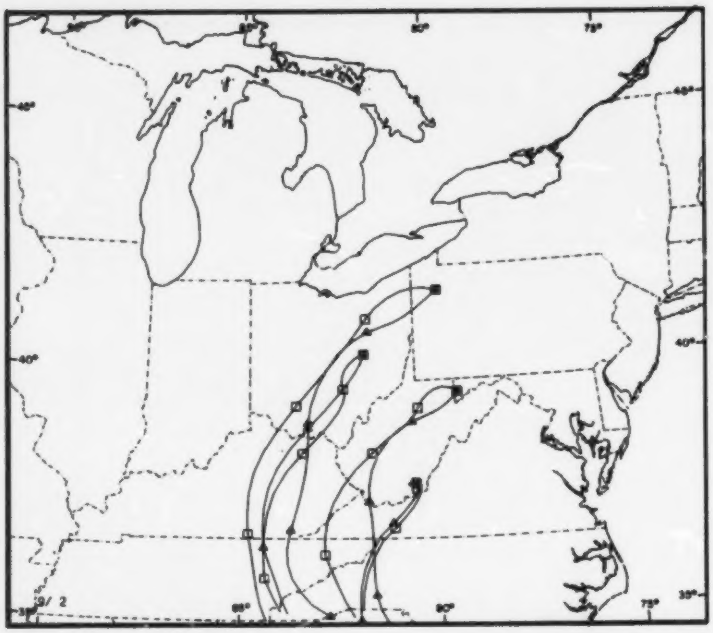
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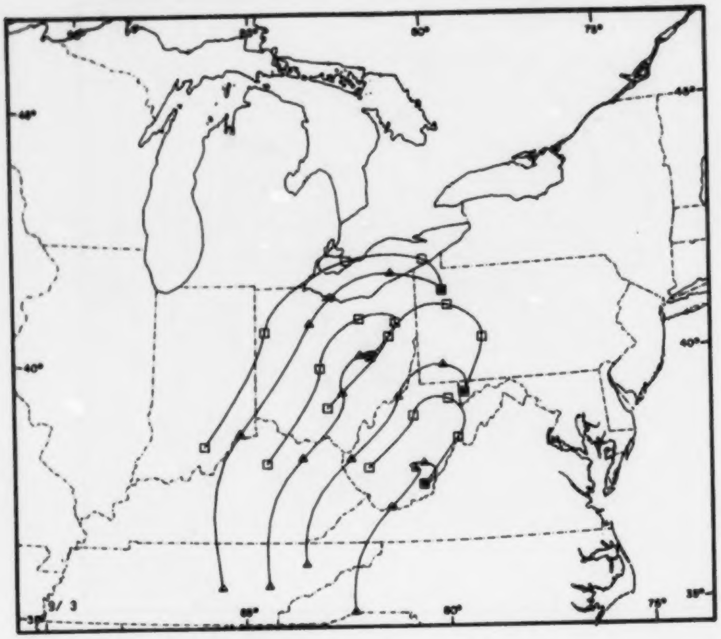
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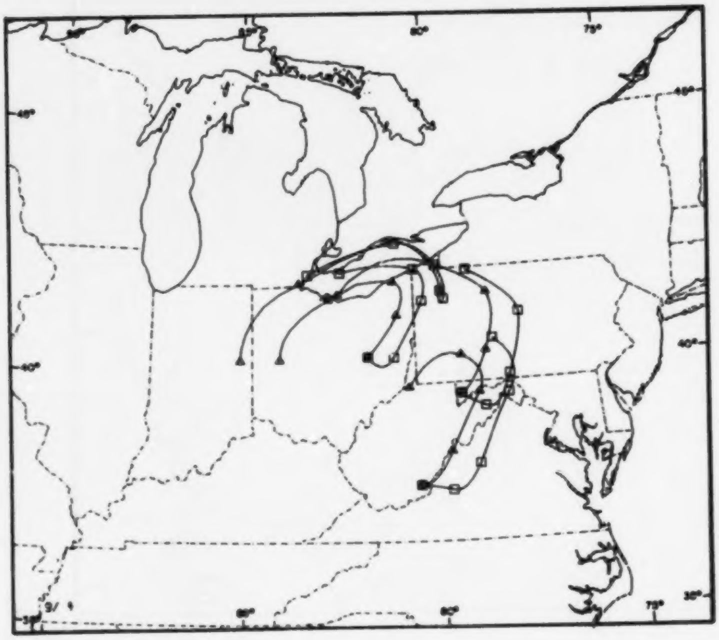
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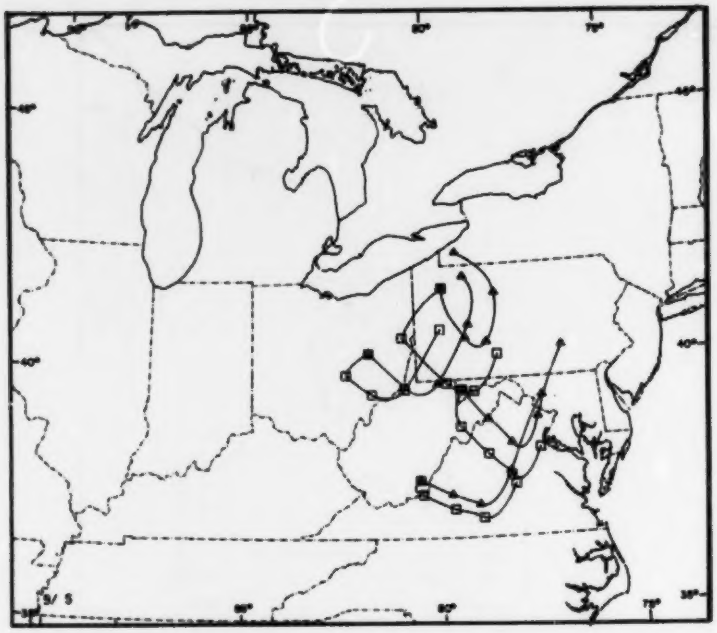

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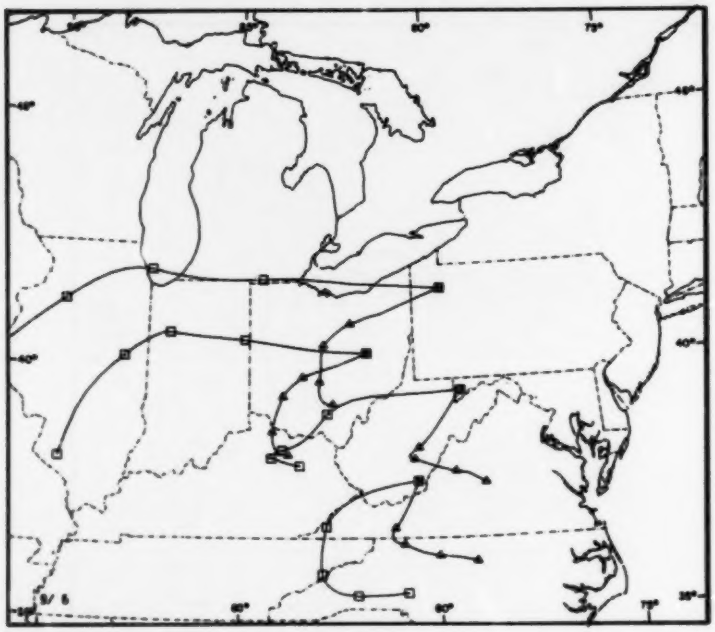

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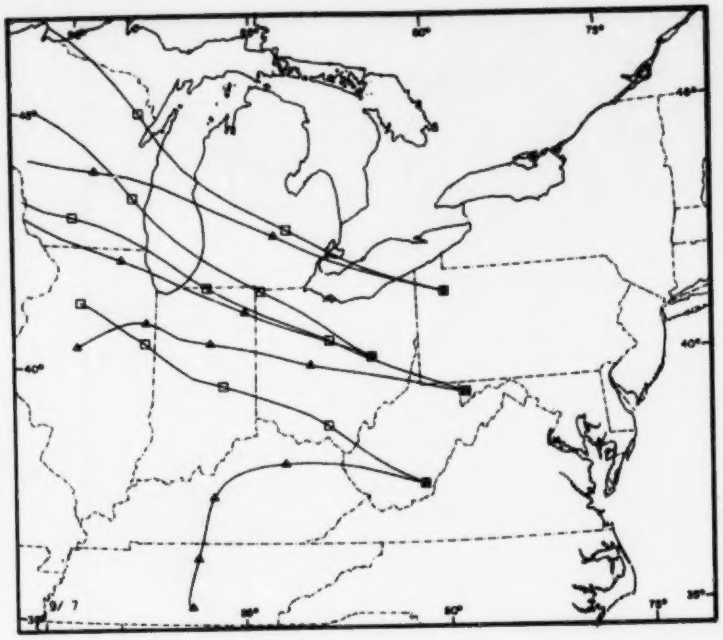
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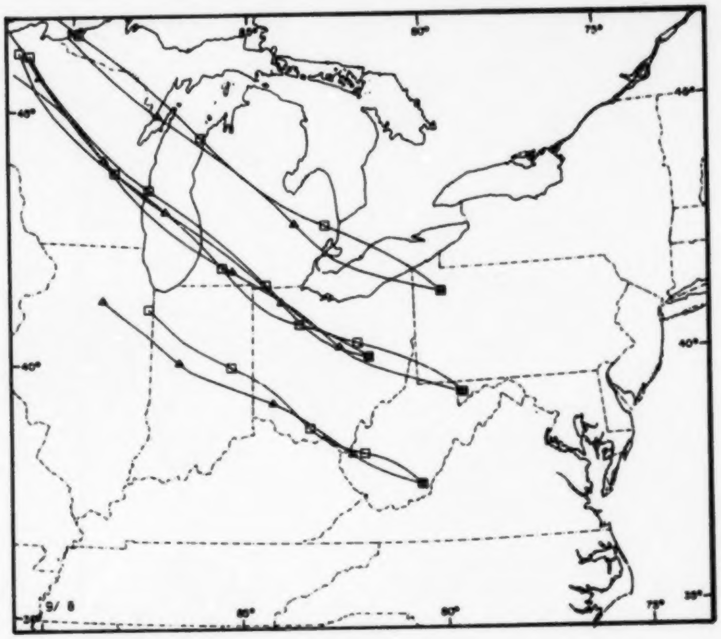
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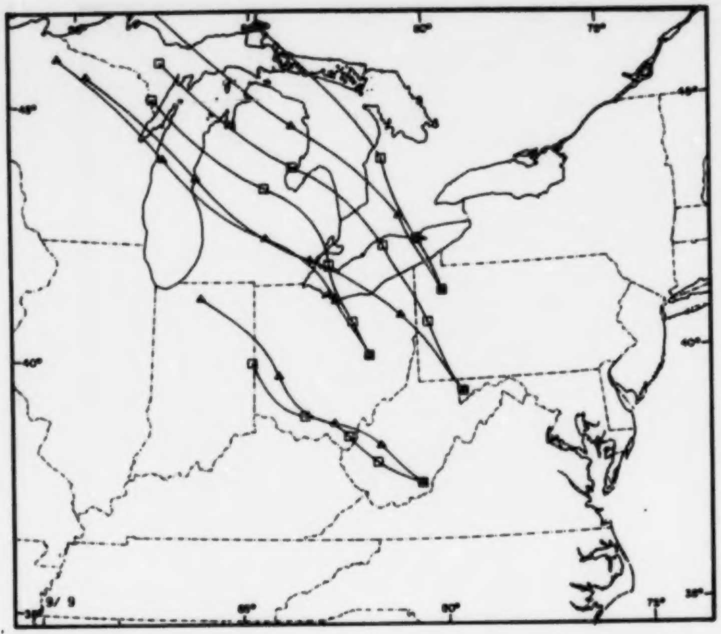
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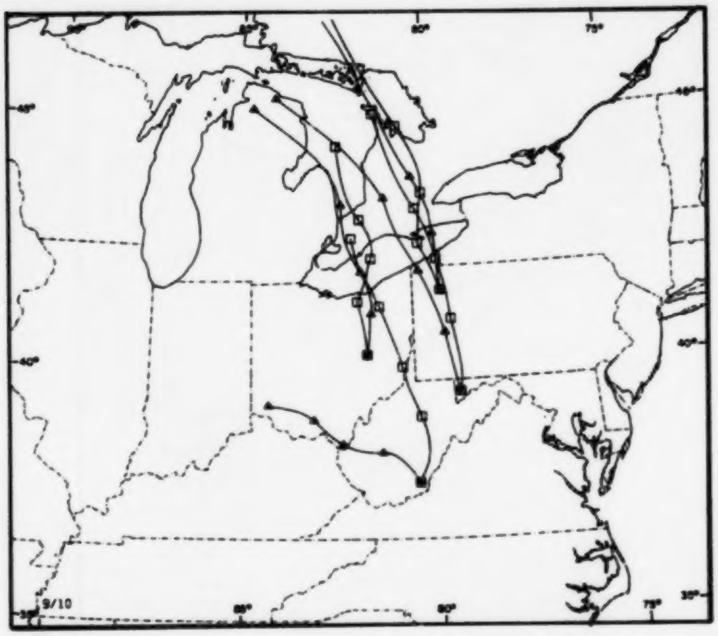
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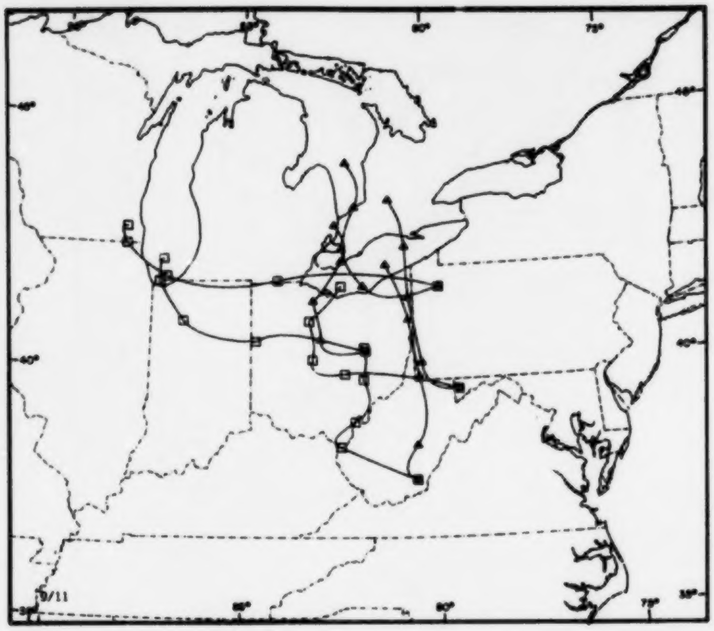
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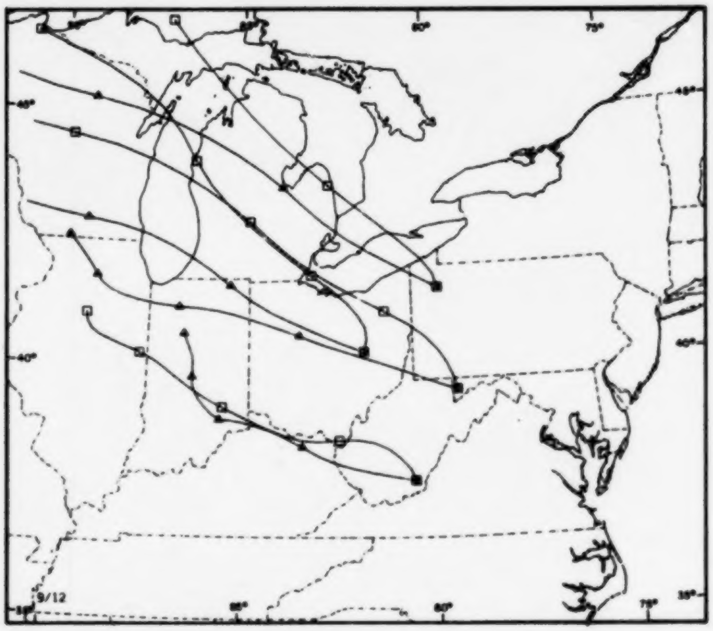
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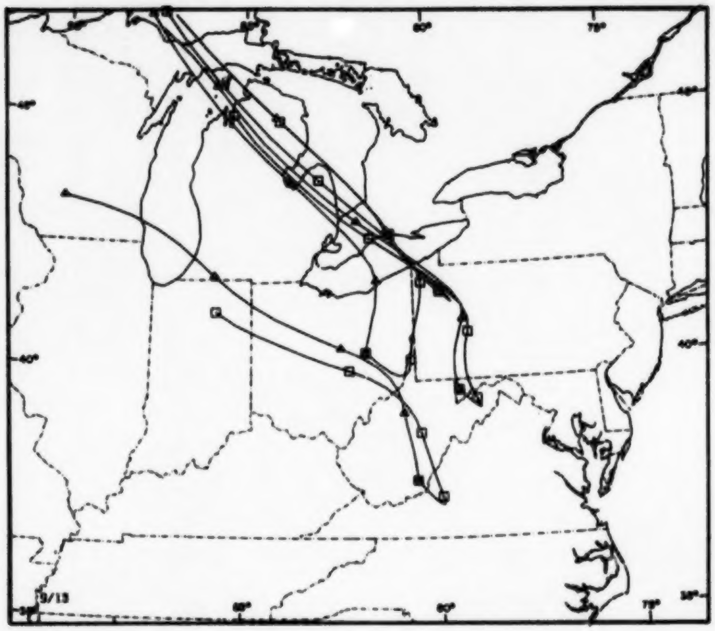
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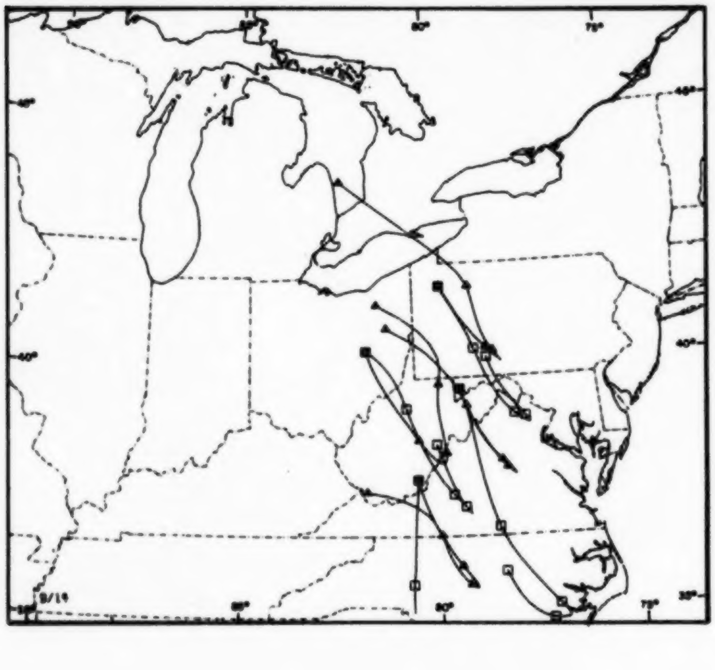
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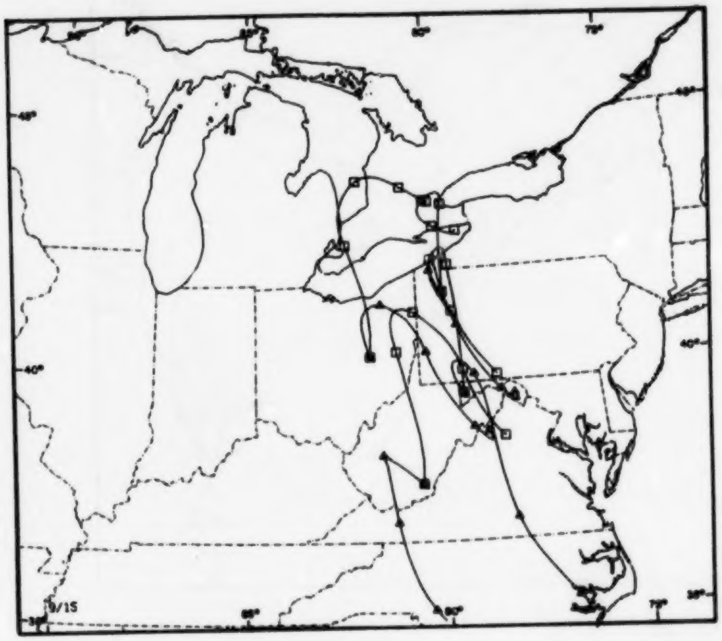
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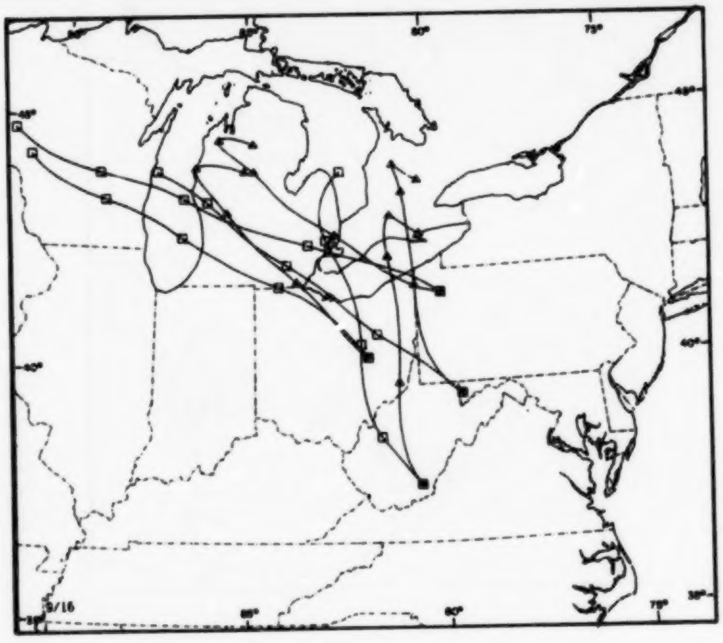
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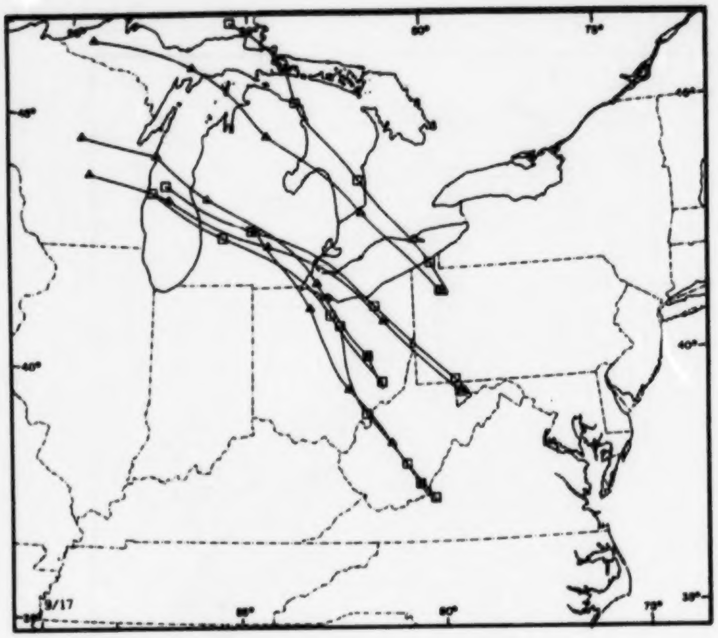

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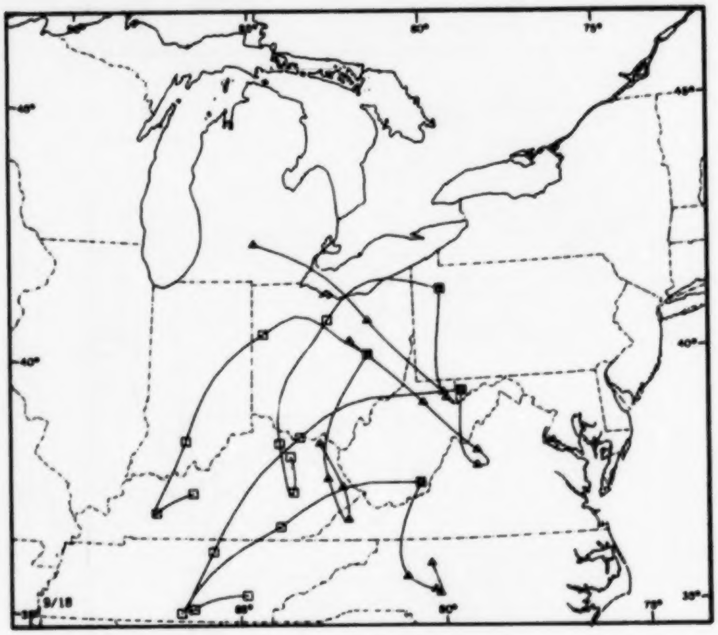

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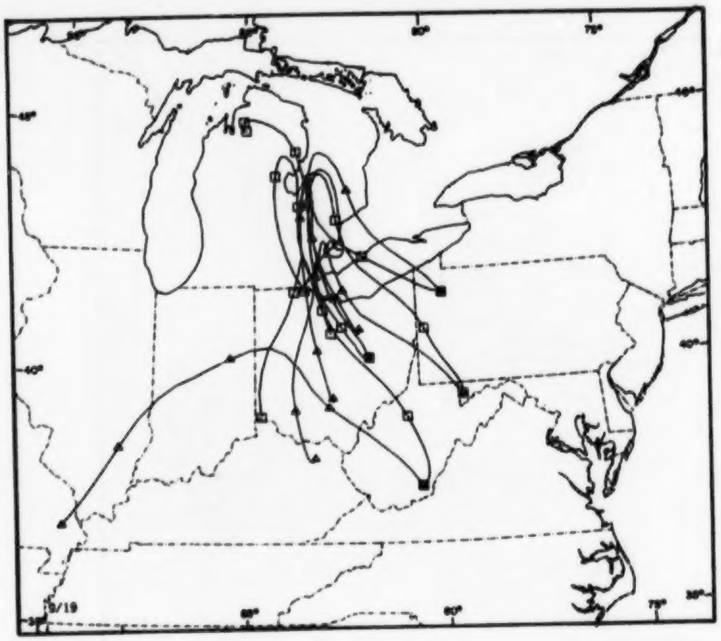
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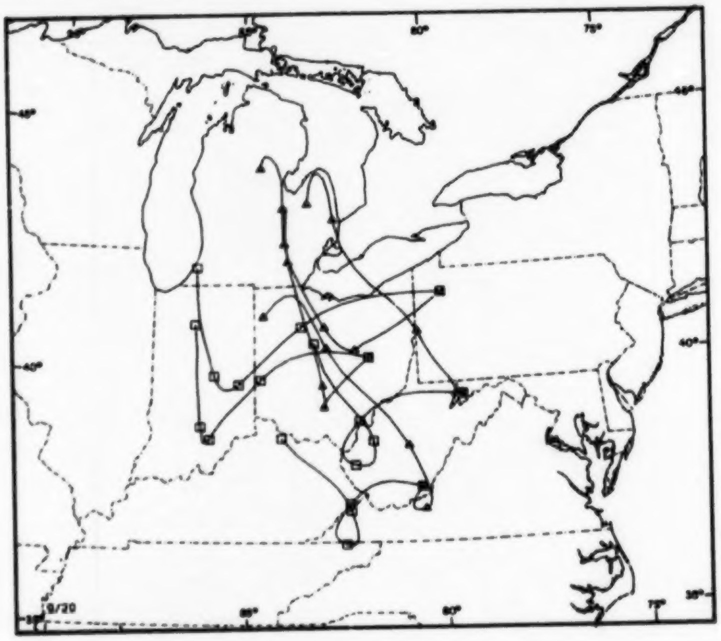
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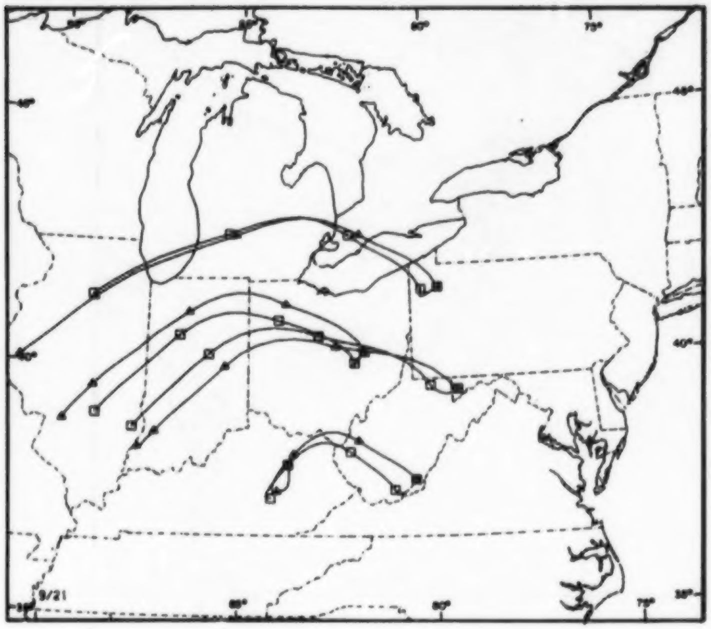
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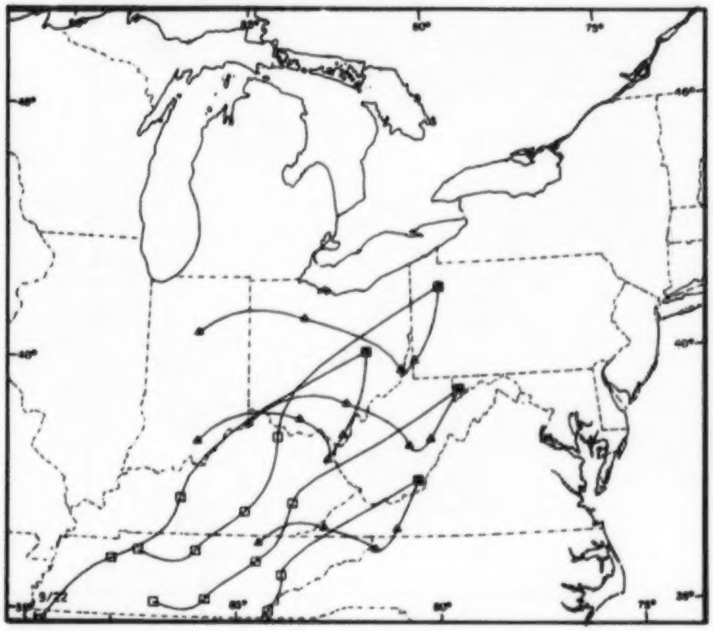
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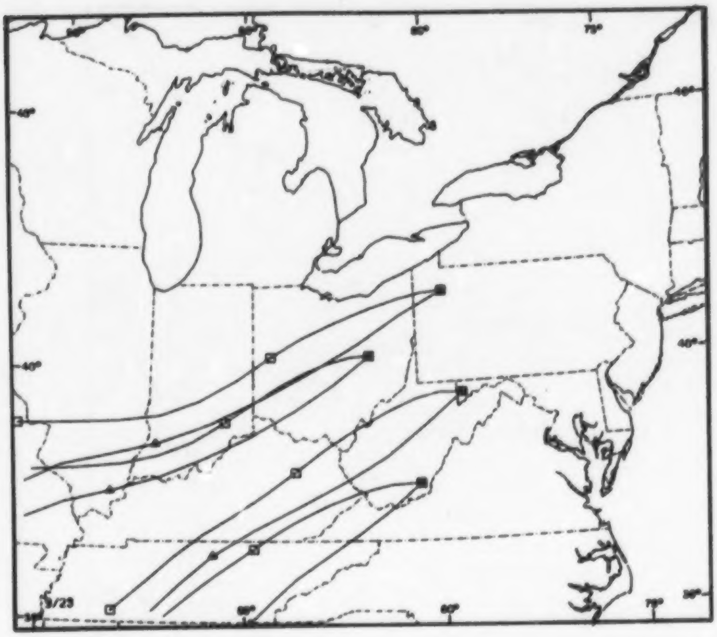
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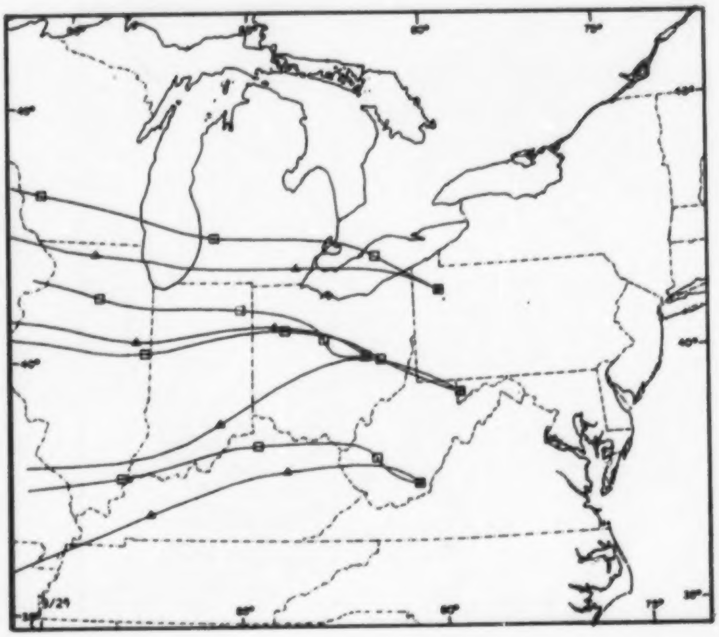
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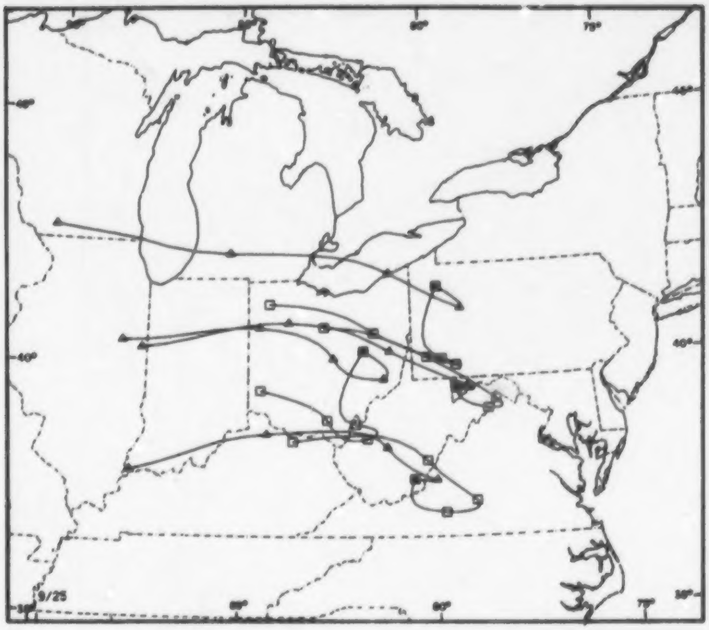

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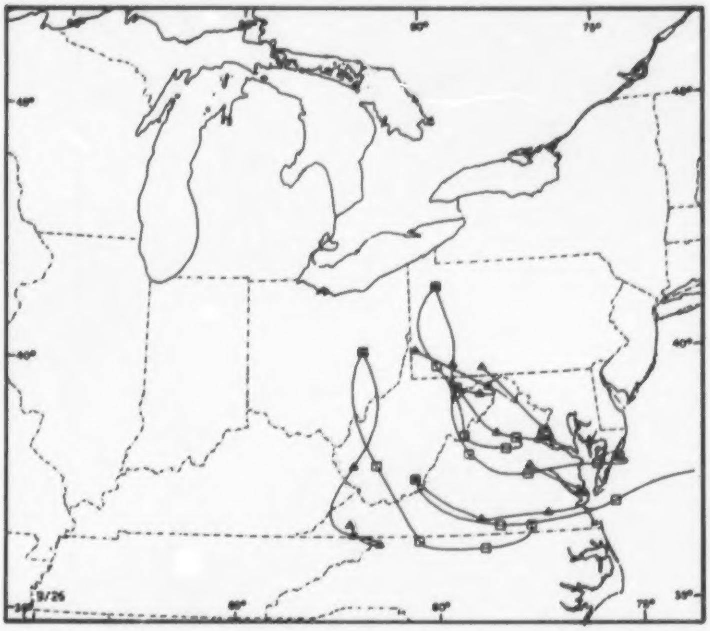

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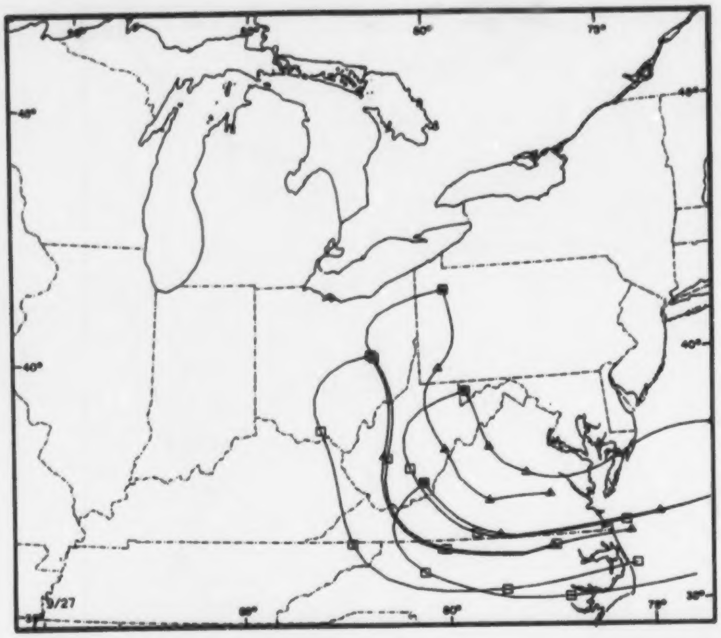
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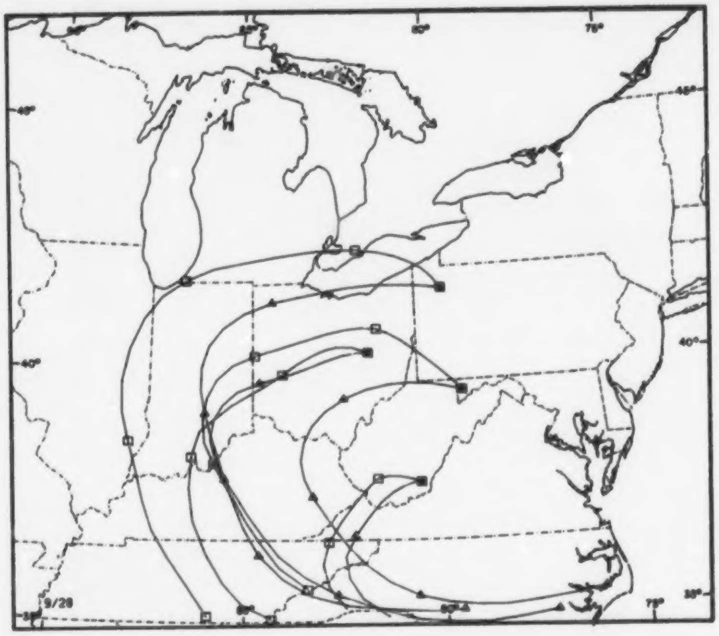
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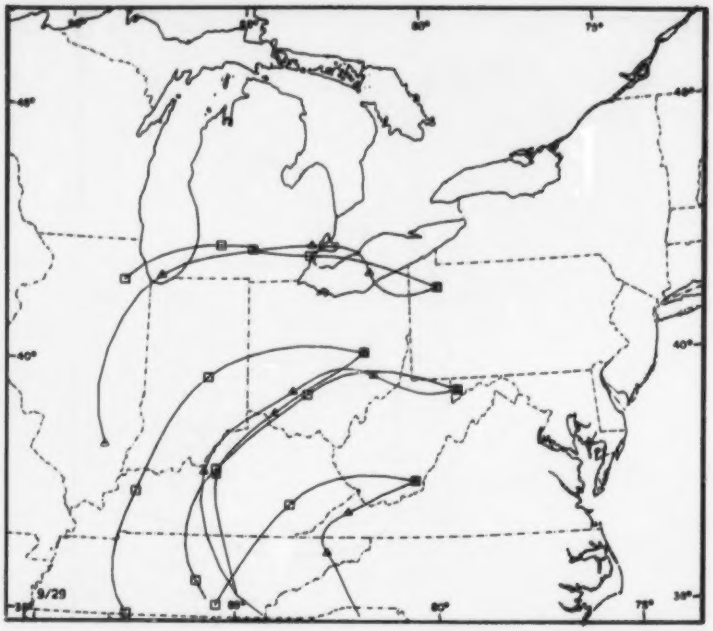
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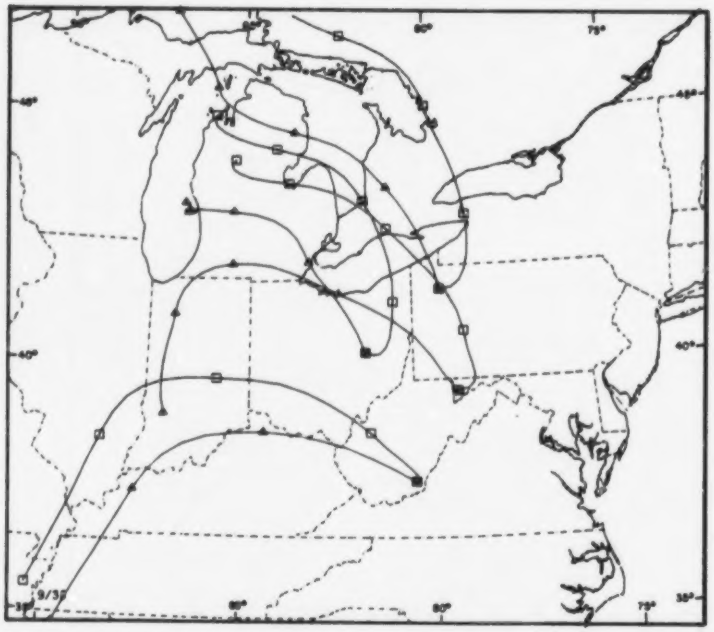
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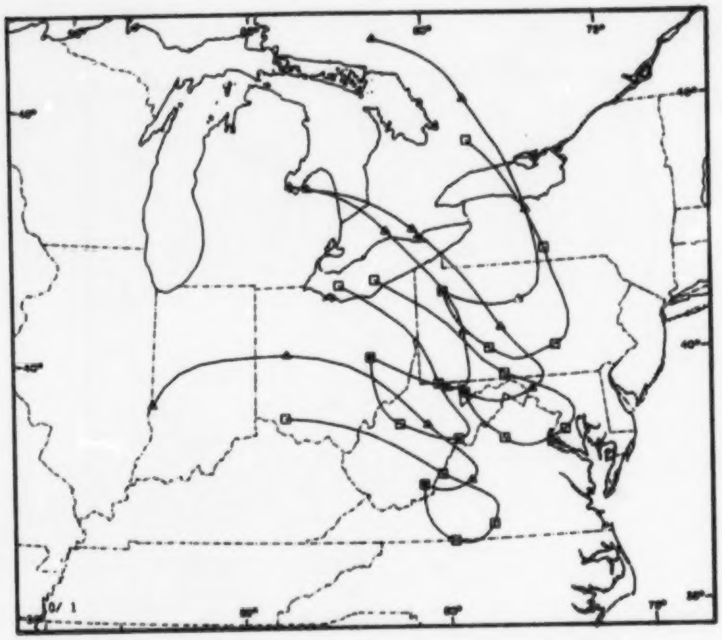

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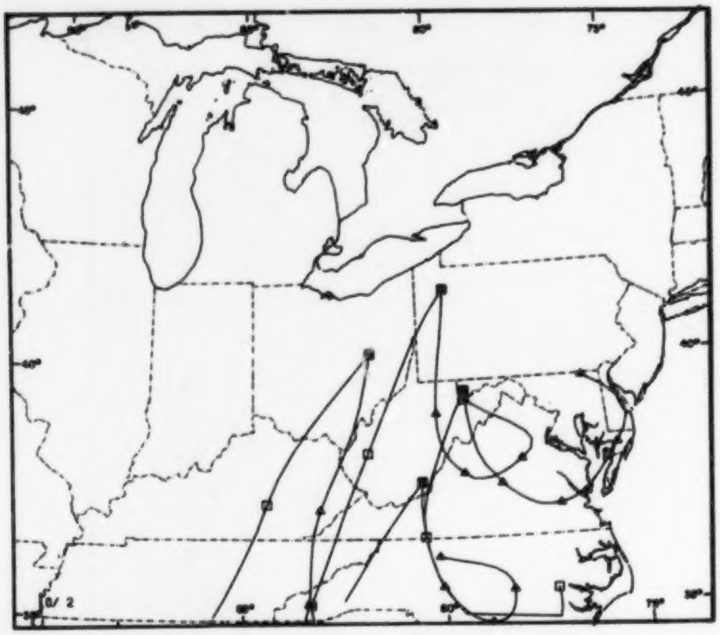
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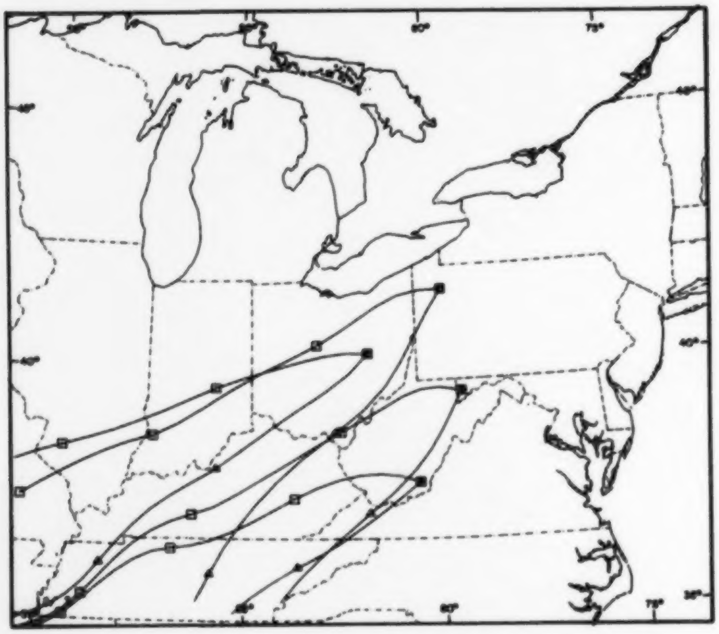
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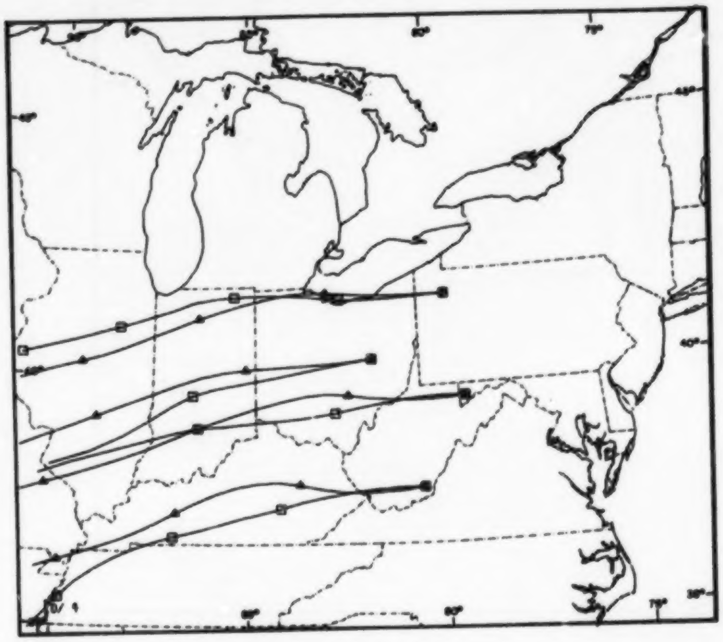

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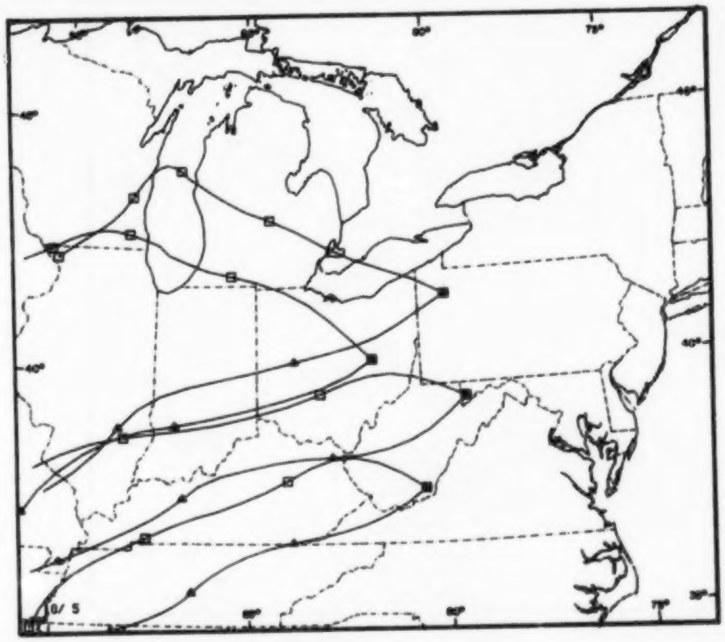

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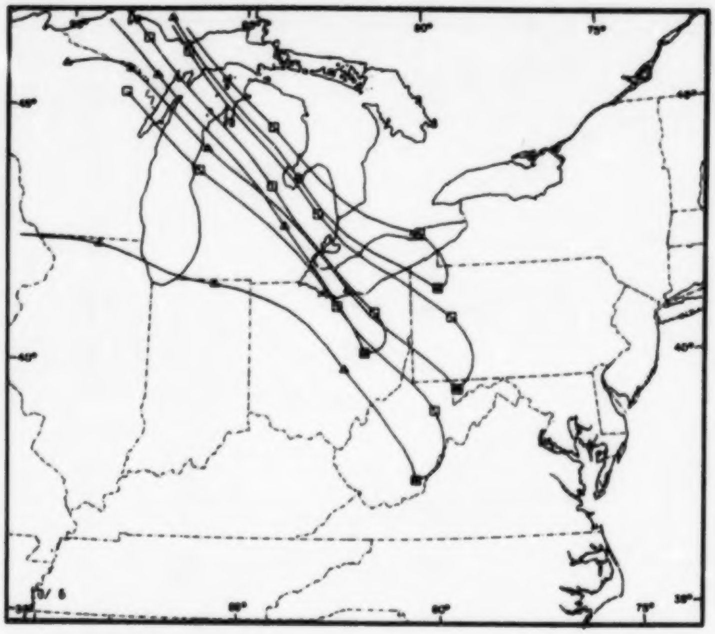
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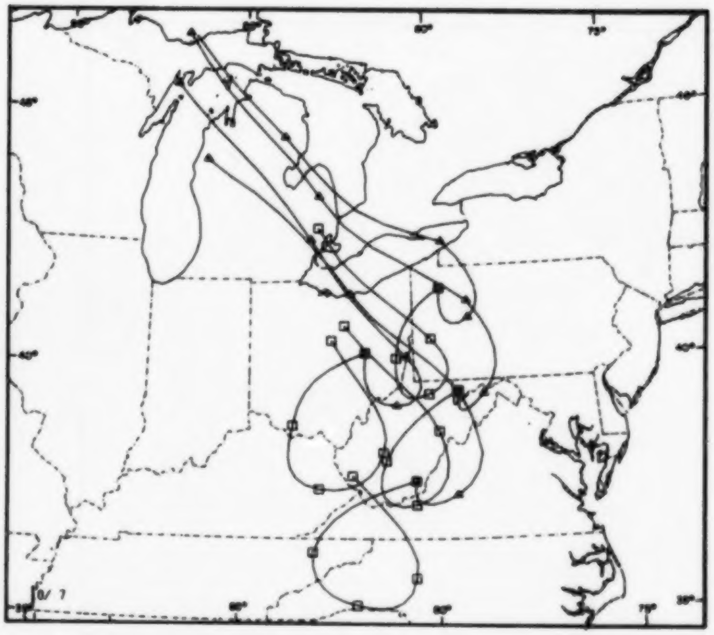
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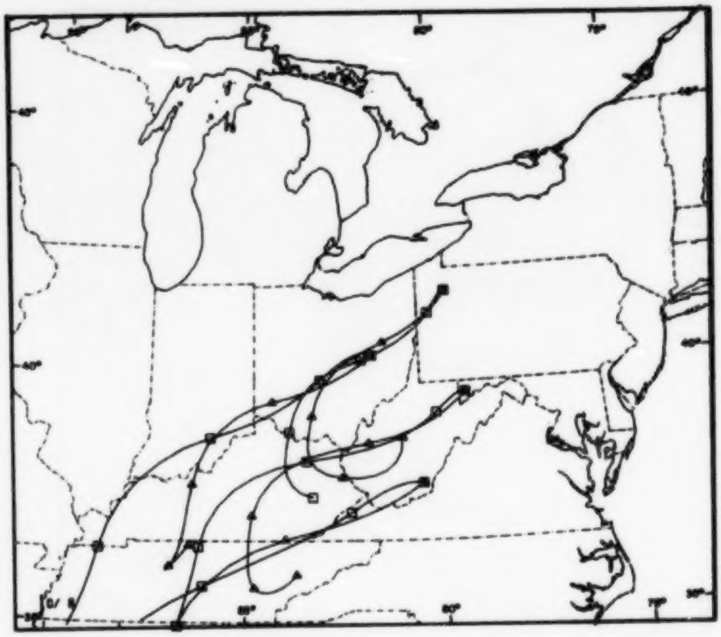
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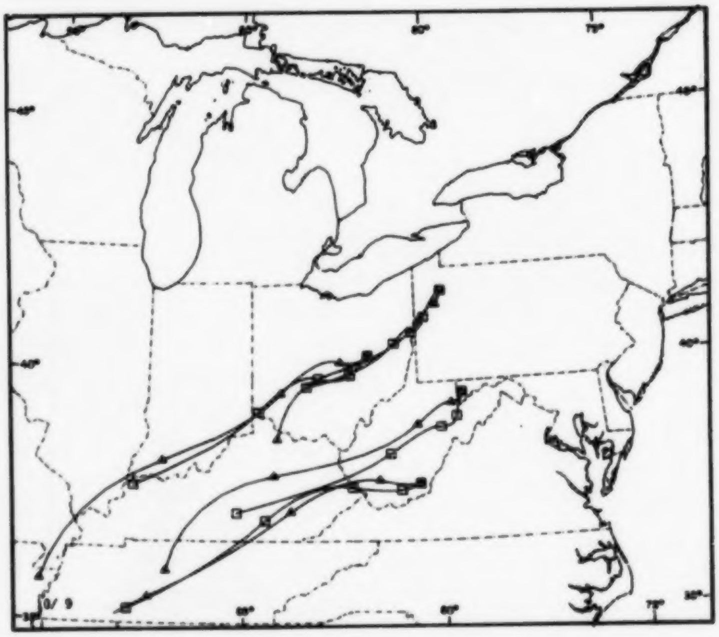
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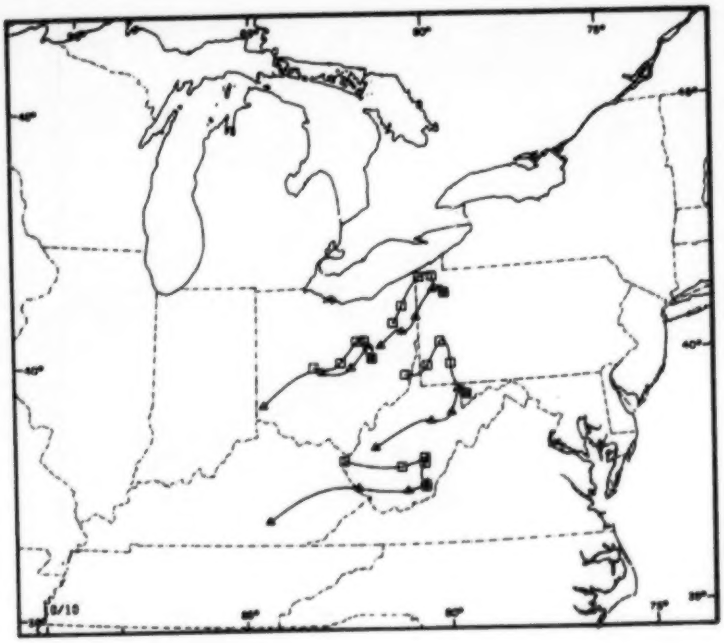
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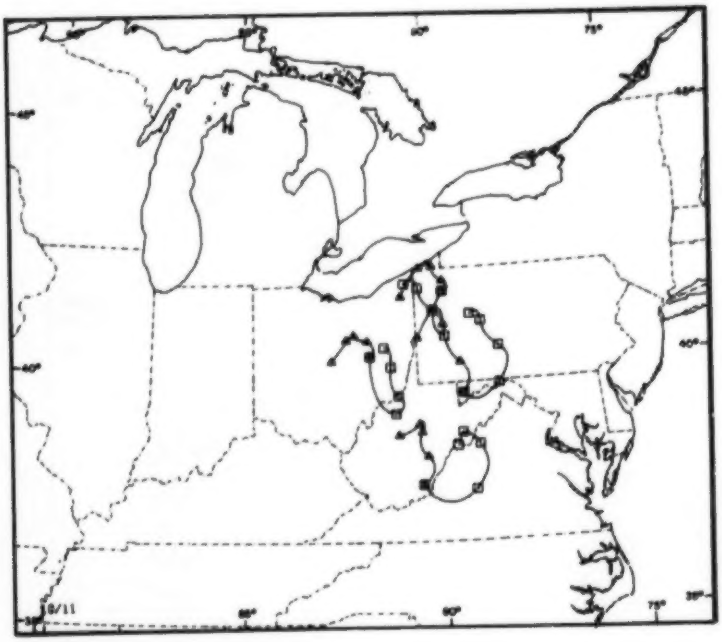
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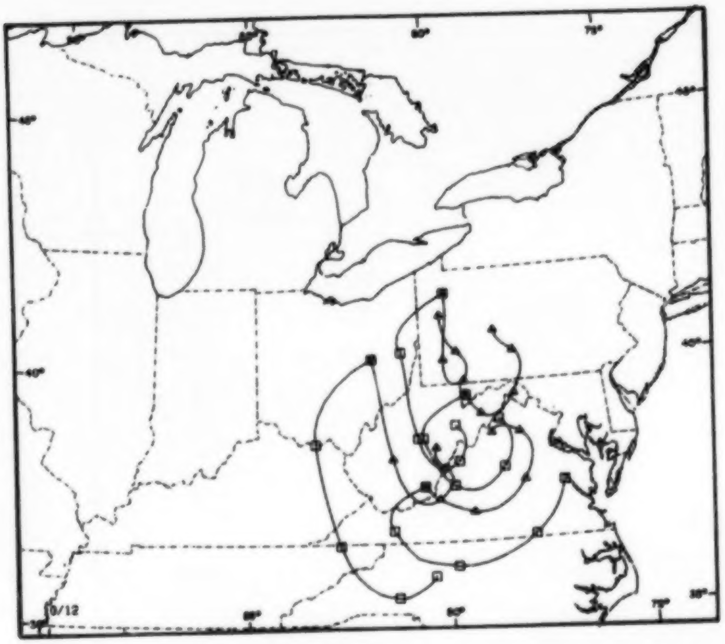
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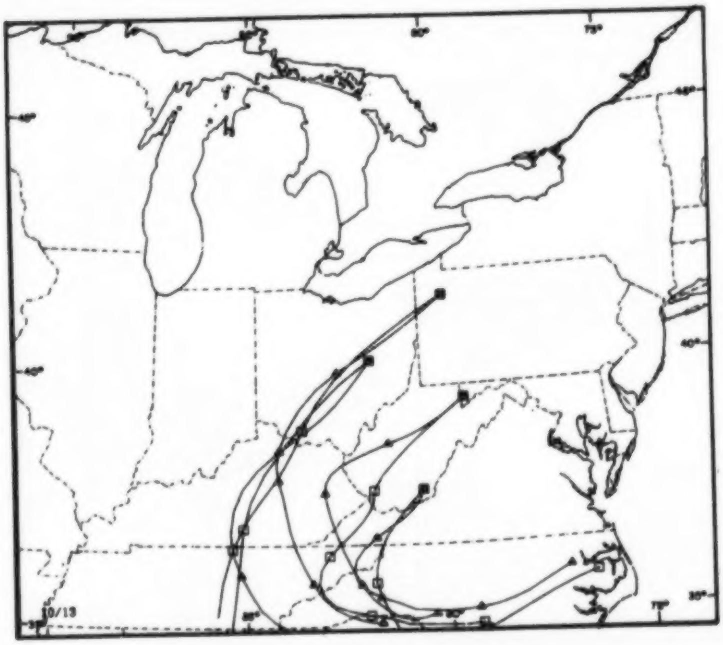
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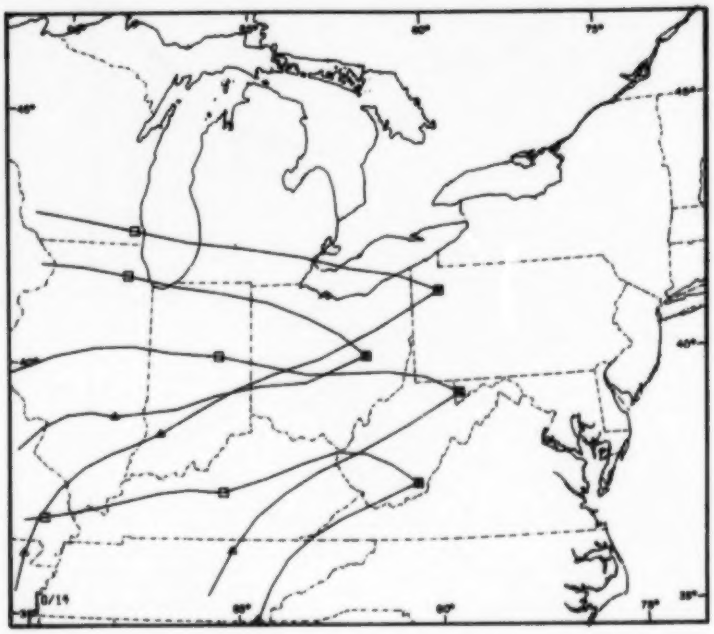
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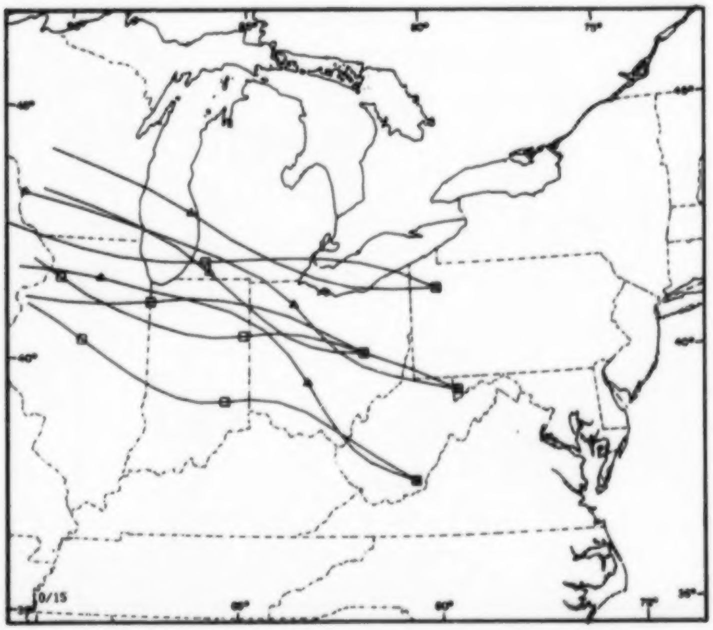
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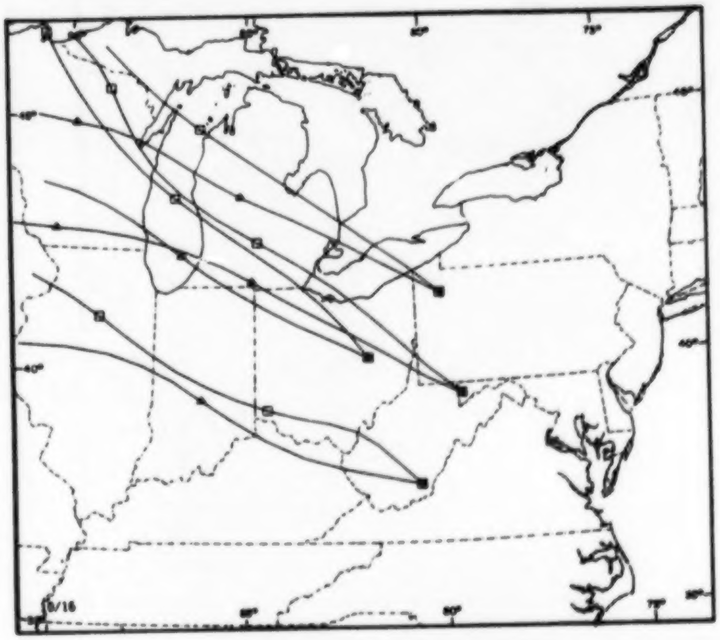
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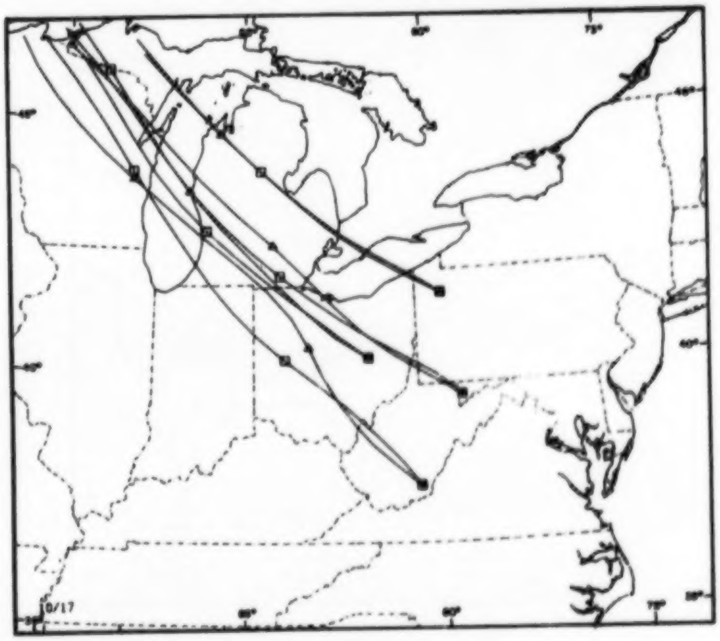
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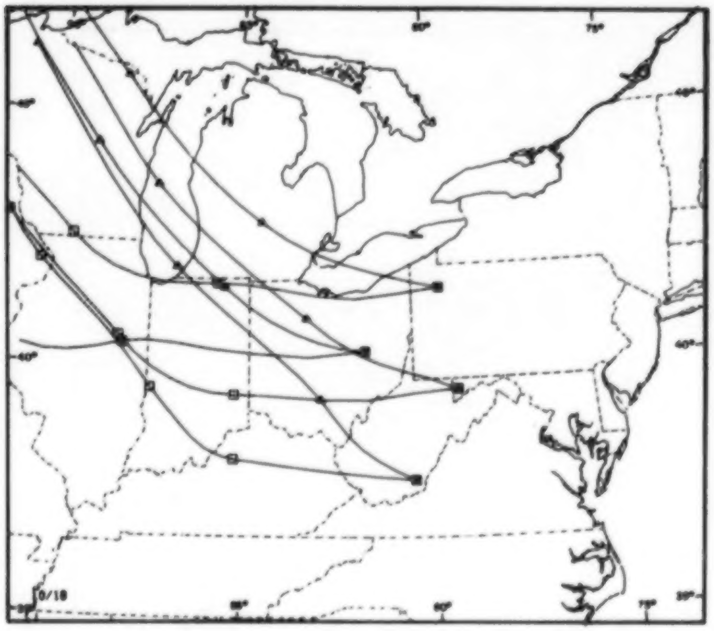
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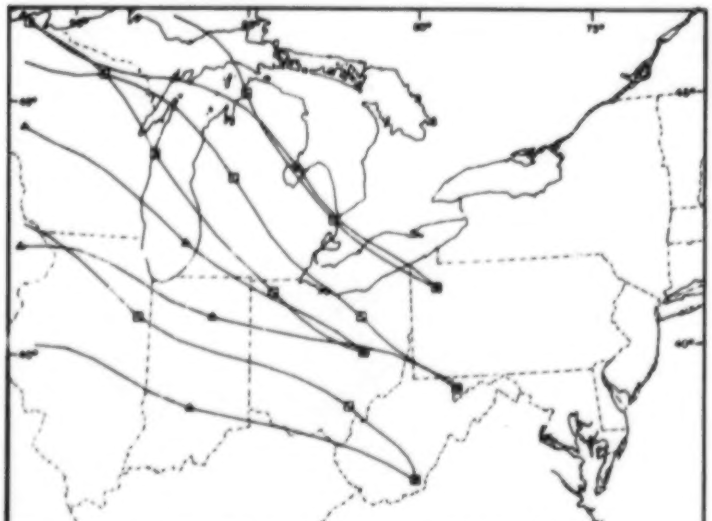
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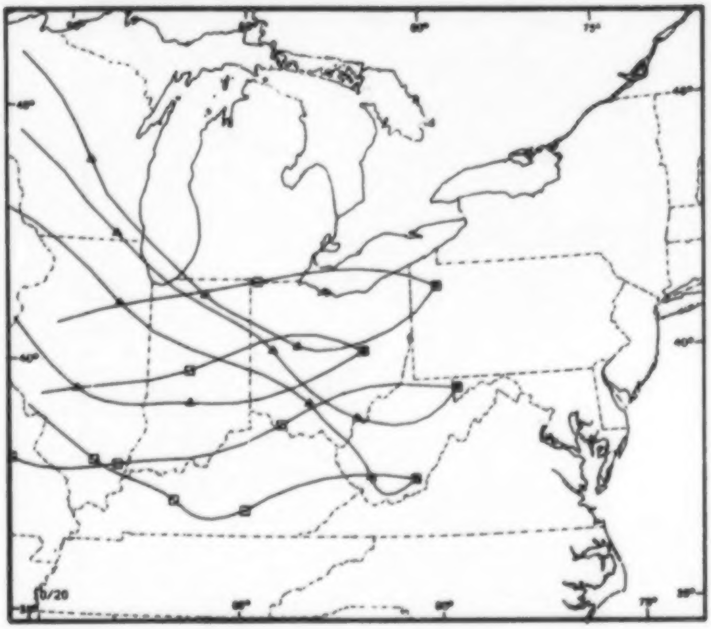
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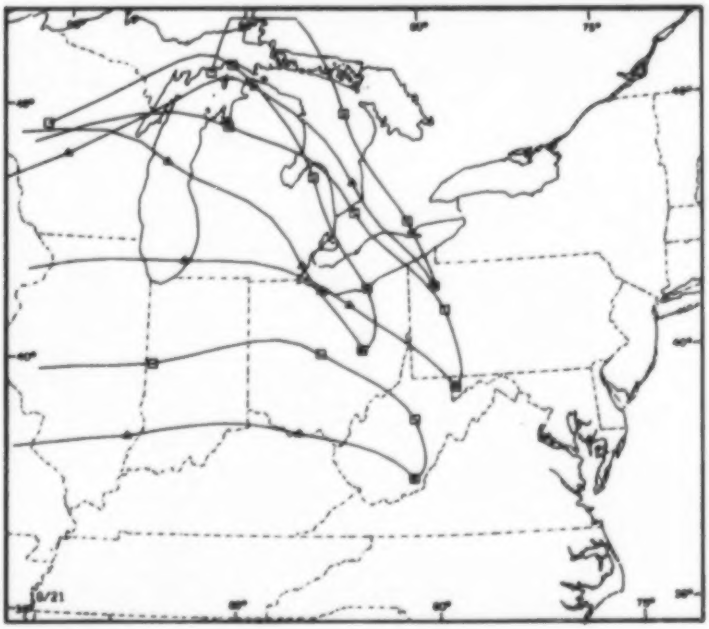
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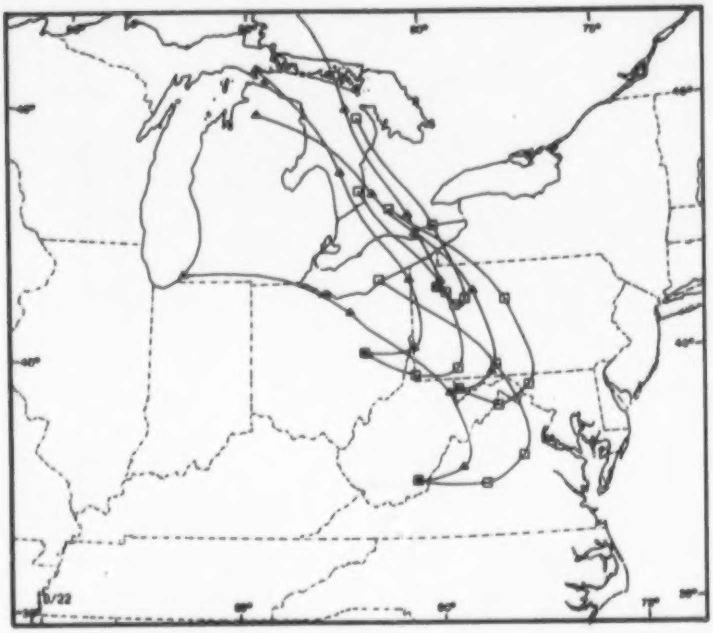
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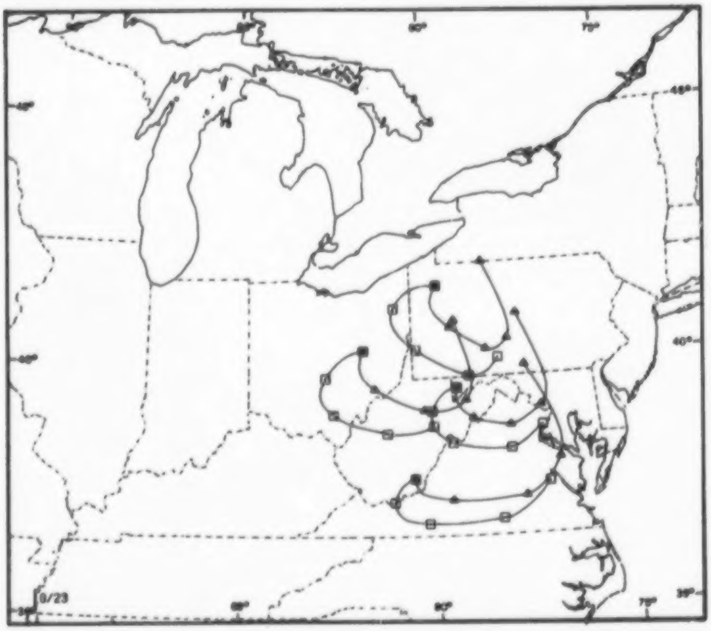
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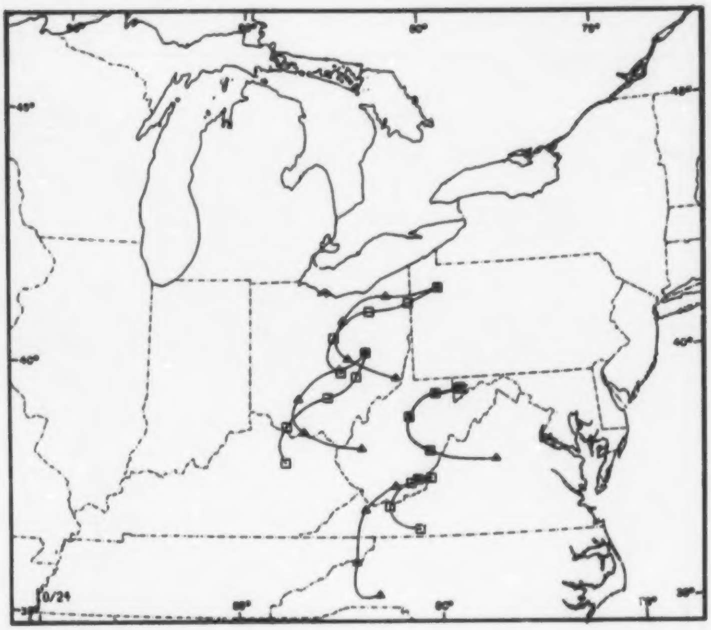
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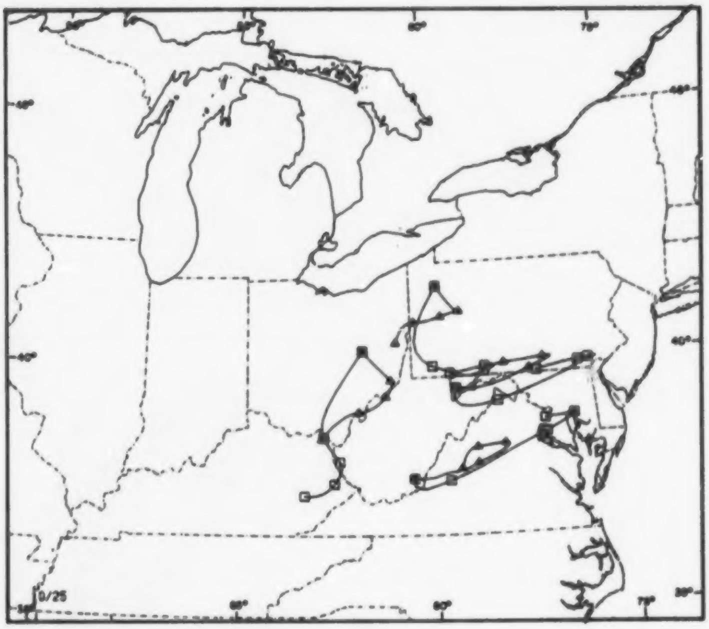
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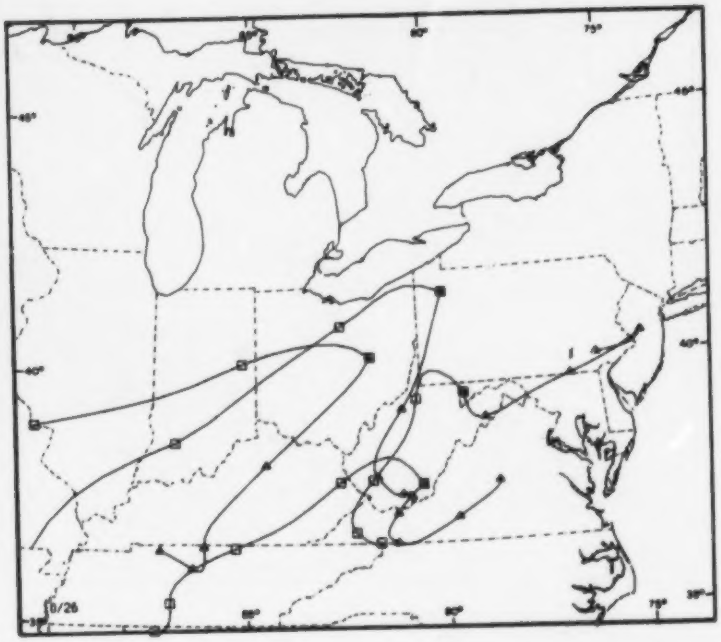
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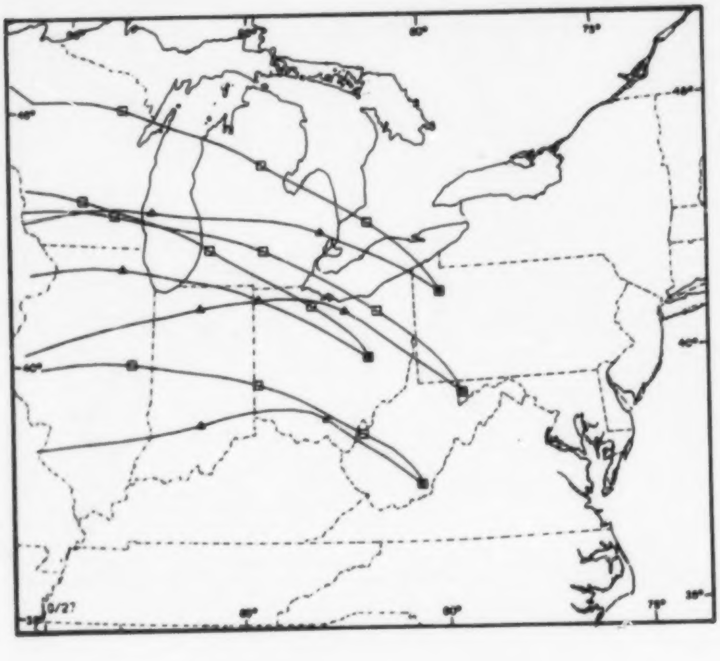
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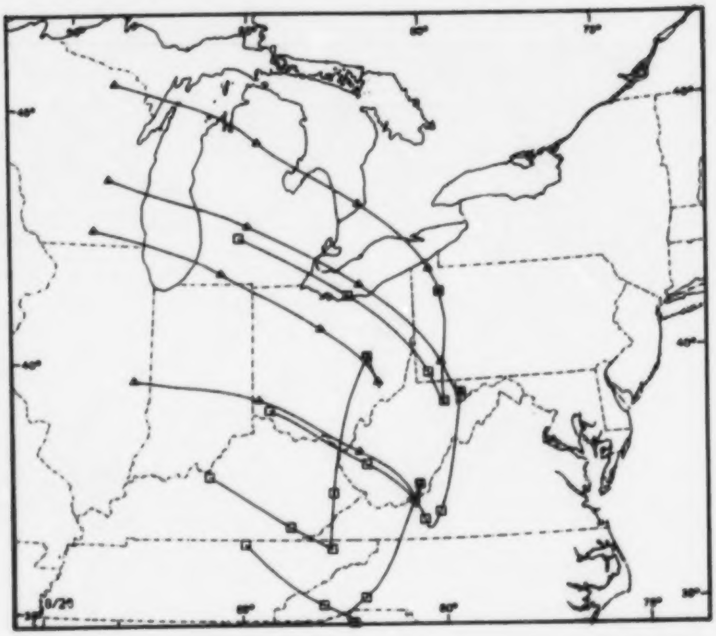
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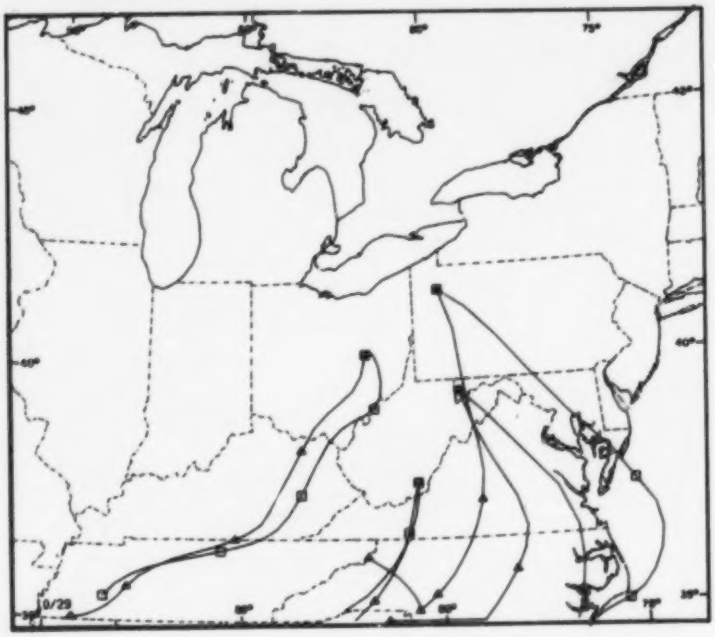
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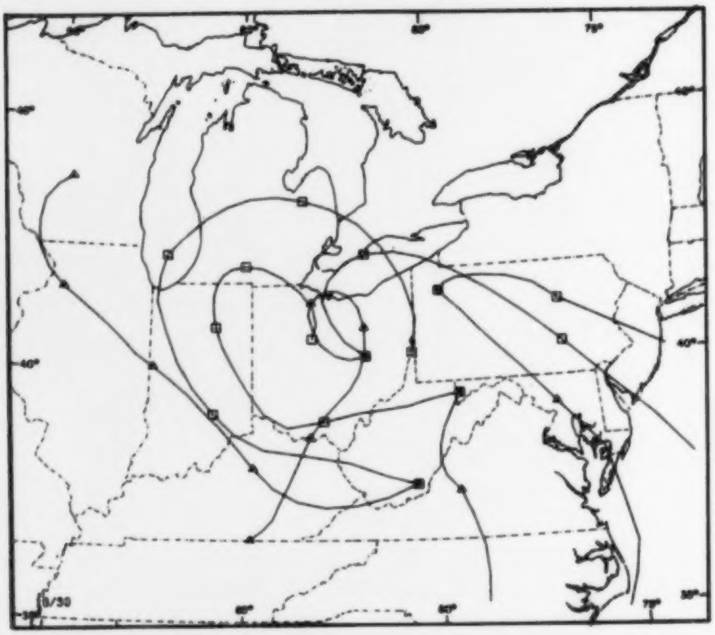
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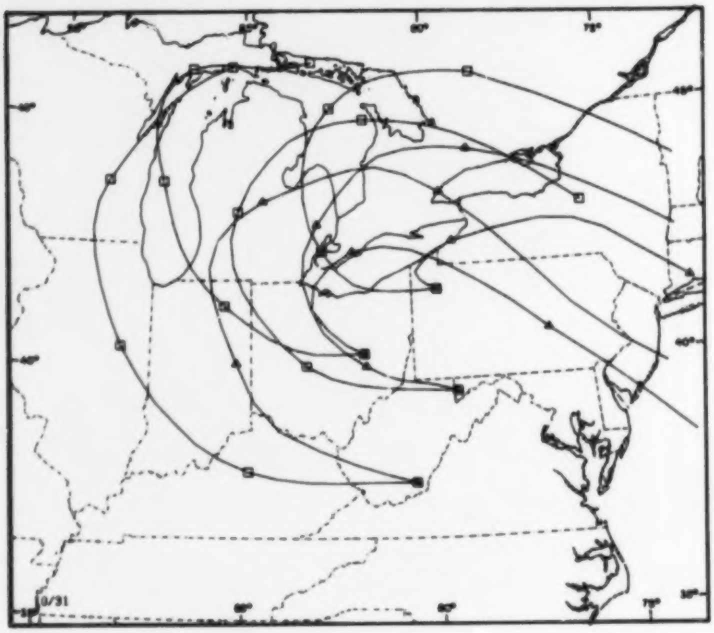
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